MICROWAVE DIGESTION OF CRUDE OILS AND OIL PRODUCTS FOR THE DETERMINATION OF TRACE METALS AND SULPHUR BY INDUCTIVELY-COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY

by

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Abstract

A study on the oil microwave digestion for determination of trace metals and sulphur in oil samples by ICP-AES was conducted by examination of the kinetic relationship of microwave digestion processes with different crude oil types, the mechanism of C_6 hydrocarbon digestion reactions, and the recoveries of metals and sulphur during microwave digestion. The oil microwave digestion and ICP-AES measurement techniques developed in this study have been applied to more than 110 different oil samples for determination of 19 elements including Ni, V, Ti, Pb, Mn, Ba, Zn, Sr ,Se and S.

RÉSUMÉ

Une étude de la digestion d'hydrocarbures par les micro-ondes pour le dosage par SE-PIHF des métaux à l'état de traces et du soufre dans des échantillons d'hydrocarbures a été effectuée par l'examen de la cinétique des processus de digestion par micro-ondes avec différents typês de pétrole brut, du mécanisme des réactions de digestion des hydrocarbures en C_6, et des taux de récupération des métaux et du soufre au cours de la digestion par micro-ondes. La digestion par micro-ondes des hydrocarbures et les techniques de mesure de SE-PIHF élaborées au cours de la présente étude ont été appliquées à plus de 110 échantillons d'hydrocarbures différents pour le dosage de 19 éléments comprenant entre autres : Ni, V, Ti, Pu, Mn, Ba, Zn, Sr, Se et S.

Acknowledgements

Introduction

Considerable attention in recent years has been focused on the study of trace metals and sulphur content in crude oils[1,2]. Metal content can provide valuable information about the origin of petroleum, which is particularly important for dealing with spills of petroleum oils and petroleum-based products[3]. Metal content can also lead to the poisoning of catalysts used in cracking and desulphurization processes. The wide occurrence of sulphur and sulphur compounds in petroleum is a well-known problem. Many sulphur compounds are also catalyst poisons. High sulphur content in residual oils may present problems through atmospheric pollution and through corrosion in furnaces and boilers.

Few detailed studies for determining trace metals and sulphur in crude oils and their products using inductively coupled plasma atomic emission spectroscopy (ICP-AES) have been reported[1,4-8]. Most of these studies recommended direct analysis of oils using a 1:10 (w/w) dilution with xylene or 1:100 dilution for nonviscous solution. However, some common problems were encountered when analyzing crude oils and their products using xylene dilution techniques. The presence of light ends (hydrocarbons with high vapour pressure) in crude oils will cause erroneously low results. This problem could be enhanced with high wax content oils. It was also reported that continuous ICP operation for over 2 hrs with xylenes will cause the cured Viton tubing to expand. This results in an increase in sample uptake rate and therefore the intensity of the signal. Special problems could be

encountered for the determination of sulphur in oils using the xylene dilution system. It has been demonstrated that different sulphur compounds in one solvent yielded substantially different sulphur sensitivities[9]. More than 200 sulphur compounds have been identified in several crude oils[10]. In addition, the sulphur memory effects will be significant for oils containing greater than 2000 ppm of sulphur for direct ICP measurement using the xylene system[1].

The pre-treatment of the crude oil samples may be the most important technique for the application of ICP to crude oil samples. Microwave digestion methods have been recently developed and the application to botanical, biological and food samples has been widely reported[11-14]. To date, the application to geological samples was mainly limited to ore samples. The application of microwave digestion to crude oil samples is infrequently reported and has not been systematically studied. Combination of the microwave digestion of oil samples with ICP measurement may provide a better method for the determination of trace metals and sulphur in oils.

It is well known that crude oil is not a uniform substance and its characteristics vary widely from oilfield to oilfield and even from well to well in the same oilfield. For example, the dynamic viscosity can vary from less than 10 c.P. to more than 10^5 c.P. at 15°C. Similarly, the densities, hydrocarbon compositions, metal and sulphur content vary widely for different types of crude oils. Therefore, for oils with widely ranged characteristics, it is not a simple task to develop a rapid and safe microwave digestion method with satisfactory recoveries.

Most commercial microwave digestion equipment, although designed for simultaneous digestion of 6 or 12 samples, can only monitor one sample for pressure. If several different types of crude oil were digested simultaneously in one microwave digester, the pressure in some samples could rise to values much higher than that of the sample being monitored. The pressure could actually rise to the point of vessel failure or explosion. On the other hand, the pressure in some vessels may be much lower than that of the pressure monitored, leading to incomplete digestion.

The present study was designed to focus on the kinetic relationship of microwave digestion processes with different crude oil types, then on the recoveries of metals and sulphur during microwave digestion. The oil microwave digestion and ICP measurement techniques developed based on this study have been applied to more than 110 different oil samples.

Experimental

Microwave digestion experiments were carried out with a commercial unit, Model MDS-2000 from CEM Corporation, which can be operated at 0-100% of full power (630 Watts) at frequency of 2450 MHz. The unit is equipped with a digital computer to control and pre-program heating rate, venting speed and pressure conditions inside the sample vessel. Closed Teflon PFA-Lined digestion vessels (100 ml) were used for crude oil digestion. Maximum operation pressure and temperature were designed to be 200 psi and 250°C. The pressure-time curves can be displayed on an interim screen or the data can be

printed out. The kinetics observed and treatment of the data is similar to that previously described[15]. A Cary-1 UV-Visible Spectrometer was used to obtain UV spectra of the solution before and after microwave digestion. The gas phase products (NO_x, CO, CO_2 and hydrocarbons) formed during microwave digestion reactions were examined by automobile emission analysis equipment. The recoveries of sulphur and metals at different oil microwave digestion conditions were measured by ICP-AES, Model 3410, from ARL. The unit is equipped with a minitorch and is operated at a radio frequency of 27.12 MHz and incident power of 650 Watts. Argon flow rates were controlled at 7.5 L/min. for coolant, and 0.8 L/min. for plasma and carrier respectively. BDH Aristar nitric acid (70%) was used for sample digestion. More than 110 different oil samples from the oilfields of the world were collected and microwave digested for ICP measurement.

Results and Discussion

1. Kinetic studies on the oils microwave digestion processes

For the initial experiments, 10 ml nitric acid was added to 0.4 gram of crude oil in the 100 ml digestion vessel. The microwave heating power was set at 378 Watts (60% of total microwave energy). The pressure versus time curves were monitored for more than 40 different crude oils with viscosity ranging from 4.5 to 234,000 c.P. and density from 0.8 to 1.0 (both measurements taken at 15°C).

Typical results are shown in Figures 1a and 1b. These figures show that different crude oils exhibit different pressure-time dependence. For example, the pressure of the
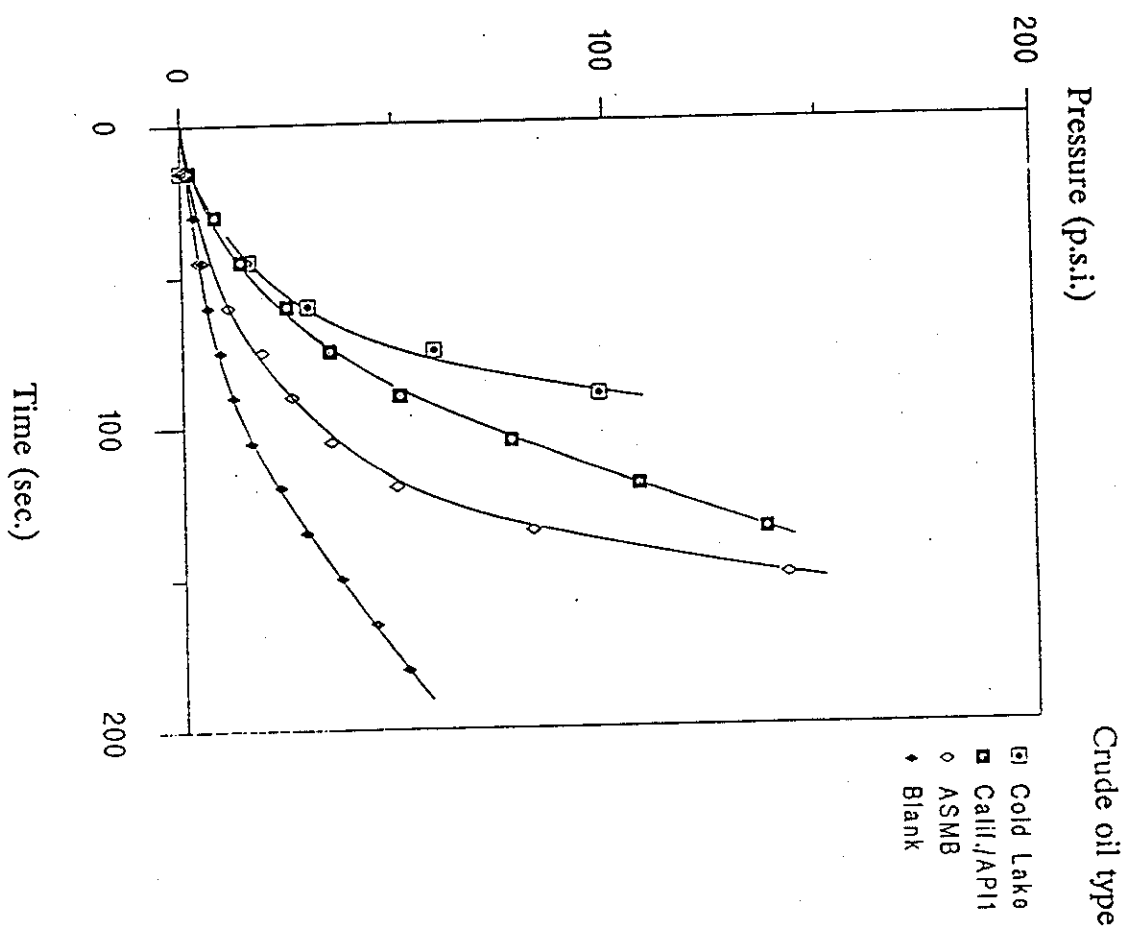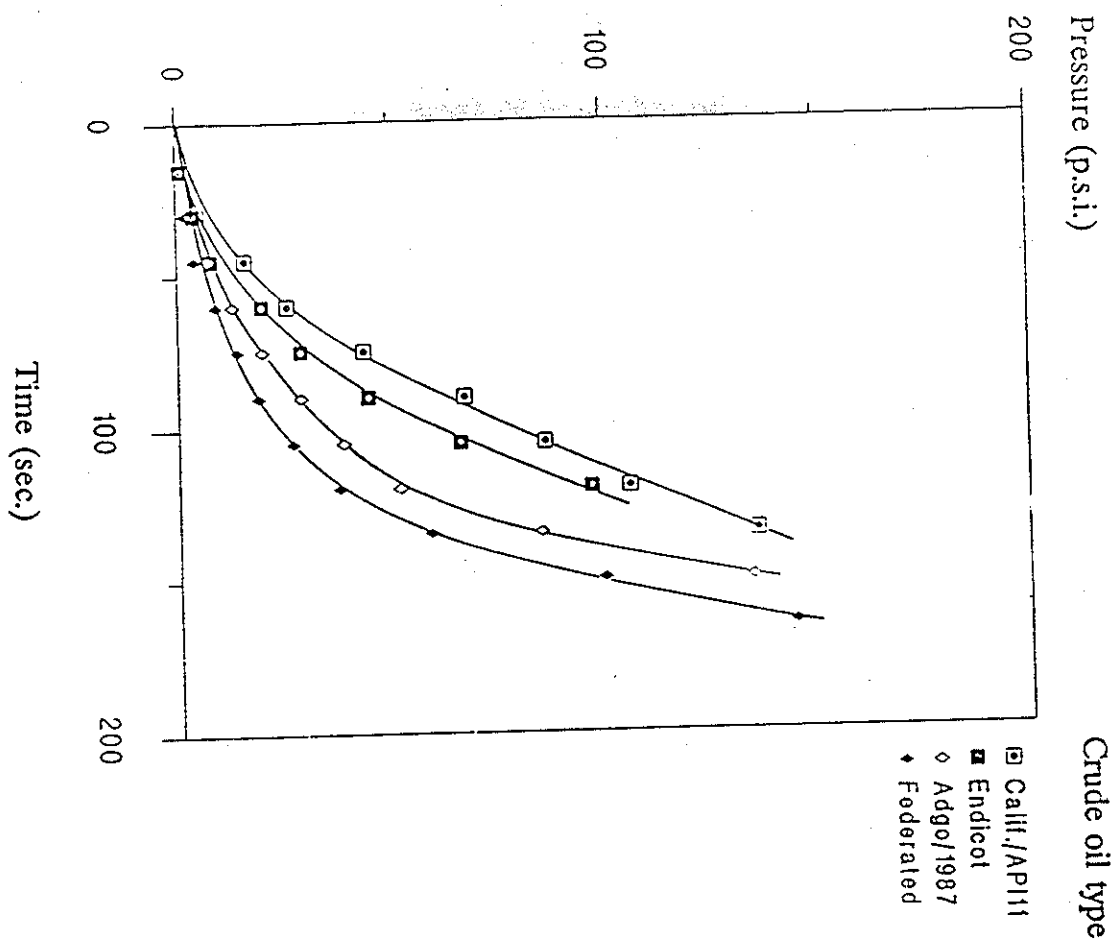
Fig.1 Pressure-time curves during microwave digestion with nitric acid

Left graph:

Pressure (p.s.i.)

Time (sec.)

Crude oil type
- ⊡ Calif./API11
- ◼ Endicot
- ◇ Adgo/1987
- ◆ Federated

Right graph:

Pressure (p.s.i.)

Time (sec.)

Crude oil type
- ⊡ Cold Lake
- ◼ Calif./API1
- ◇ ASMB
- ◆ Blank

Federated crude oil vessel rose to 40 psi at 2 minutes while, at the same conditions, the pressure in the vessel with Cold Lake crude oil would be more than 200 psi, leading to an explosion. These figures show a general trend that crude oils with high density or viscosity display faster pressure increases during the digestion process.

The microwave heating of substances is directly related to the dielectric constant of the material being treated. Nitric acid has a high dielectric constant at microwave frequencies, whereas oil has a low one. Oil is not significantly affected by microwave energy. Thus, the heating should largely depend on the amount of nitric acid present. These experiments were performed with 10 ml nitric acid and 0.4 gram of crude oil samples. The absorption of microwave energy during the digestion, particularly in the early stages, should be almost the same for different oil types. The differences in the pressure-time curves for different crude oil samples, as shown in Figure 1, reflect the differences in kinetics and mechanism of the reactions between nitric acid and oil samples and not the microwave absorption differences. Although the reactions between nitric acid and crude oils are very complicated, the initial rate of the digestion reaction can be reasonably monitored using the pressure-time dependence.

Table 1 contains the densities, viscosities, hydrocarbon compositions and the measured initial rates for different crude oil samples. Figures 2a and 2b show the relation between the initial rates of microwave digestion and the densities and viscosities of the crude oils.

The initial rate for reactions in the microwave digestion vessel can be expressed by :

$$R^{\circ} = [dp/dt]_{t=0} = k[C]^{n}[a_0]^{m}$$

Table 1 The Characteristics of Crude Oils and Initial Rates of Microwave Digestion Reactions

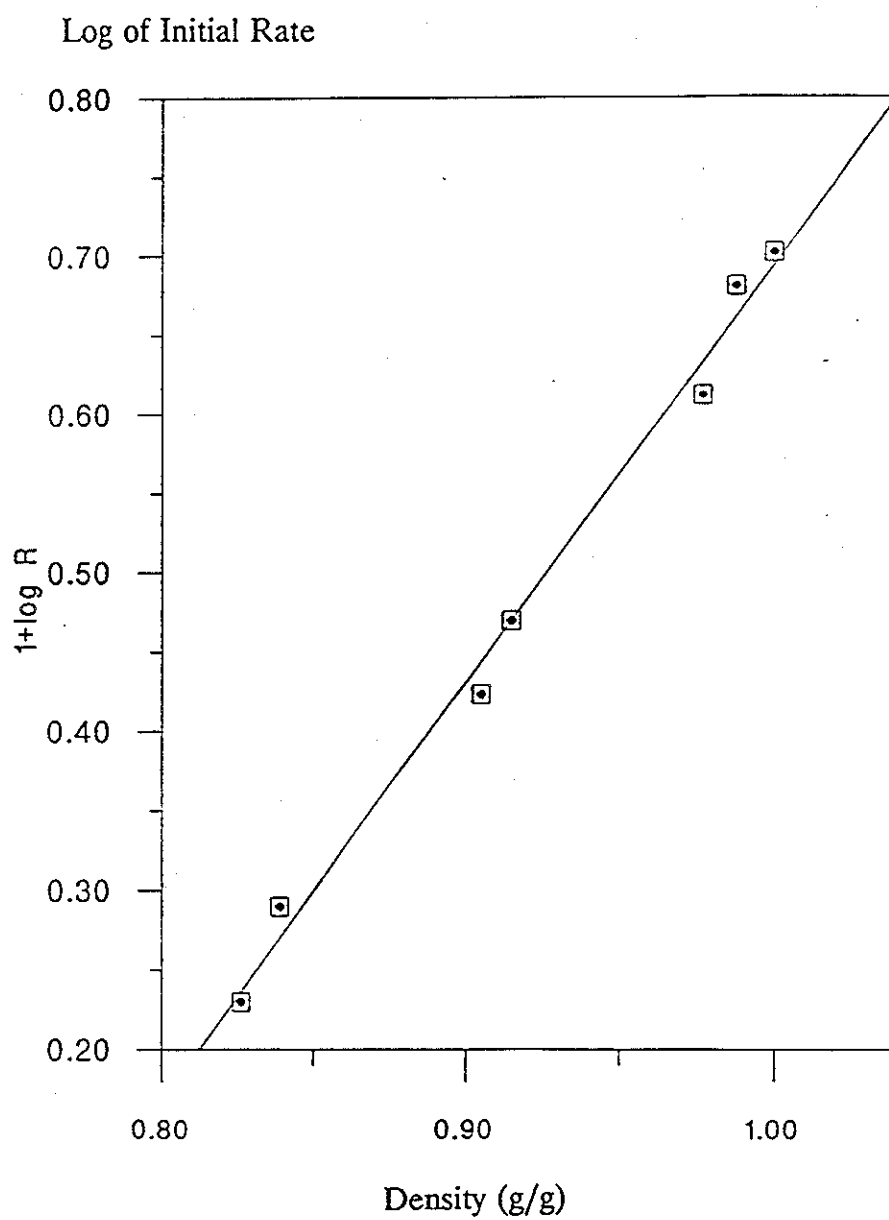| Crude Oils	Density	Viscosity/c.p.	Saturated Hydrocarbon	Aromatics	InitialRate psi/sec
Federated	0.826	4.5	87%	11%	0.17
Alberta	0.839	9.2	84.20%	12.80%	0.195
Adgo-1987	0.905	64	79.80%	18.80%	0.265
Endicot	0.915	84			0.295
California API-15	0.977	6400	13.70%	36.40%	0.41
California API-11	0.988	34000	13.70%	29.80%	0.48
Cold Lake	1.0002	235000	16.60%	39.20%	0.504

Log of Initial Rate

Fig.2a Relationship between log of initial rates and densities
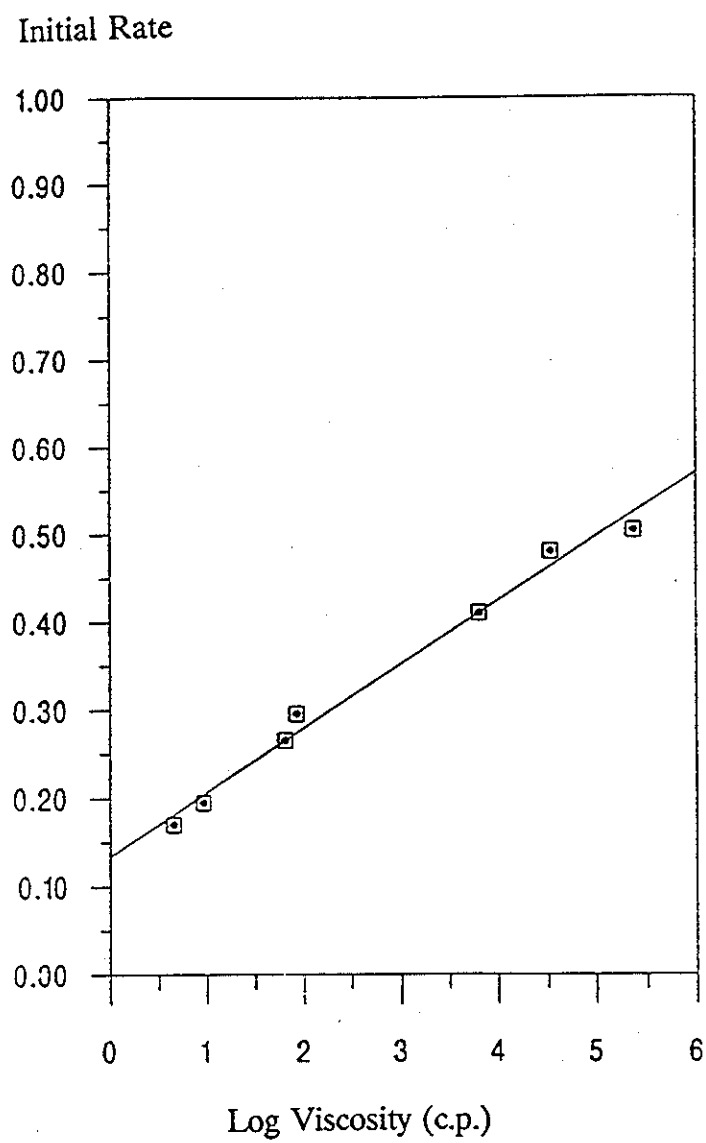
Initial Rate

Fig.2b Relationship between log of viscosity and initial rate
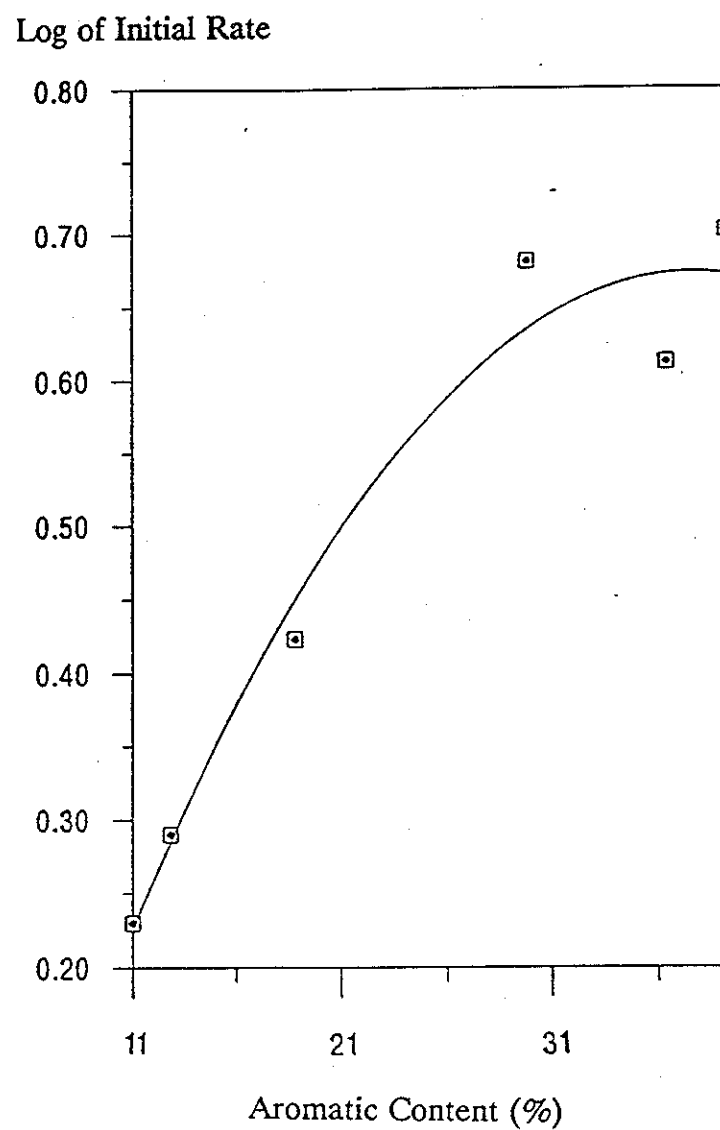
Log of Initial Rate

Fig.2c Dependence of Initial Rates on the Aromatic Hydrocarbon Contents

where p is pressure in vessel in psi

t is digestion (microwave heating) time in second

C is concentration of crude oil or the amount of oil sample added

a_0 is amount of nitric acid

n is reaction order with respect to oil concentration

m is reaction order with respect to nitric acid

In case that $[a_o] >> [C]$, the initial rate can be simplified to

$$R^\circ = [dp/dt]_{t=0} = k[C]^n$$

and $$\log R^\circ = \log k + n\log[C]$$

The reaction order with respect to oil concentration can be determined using a plot of log R° versus log[C]. Figure 3 shows the microwave digestion results for varying amounts of Cold Lake crude oil with a fixed amount of nitric acid and fixed microwave heating conditions. The reaction order with respect to crude oil amount was determined from Figure 3b to be 1.10, which is very close to first order. In principle, the reaction order with respect to nitric acid can be determined using the same method by varying the amount of nitric acid with a fixed amount of oil samples. However, the change in the amount of nitric acid will also change the absorption of the microwave energy in the reaction vessel. Therefore, the situation will be more complicated and the reaction order with respect to nitric acid can not be easily measured.

The results in figures 3a and 3b show that the reaction order with respect to the amount of Cold Lake crude oil is close to first order. Similar results were obtained for ASMB crude oil. The results of the pressure-time curves for different crude oil samples

Pressure (p.s.i.)　　　　　　　　　　Amount of crude oil (grams)

200

⊡ 0.396
▣ 0.312
◇ o.199
◆ 0.099
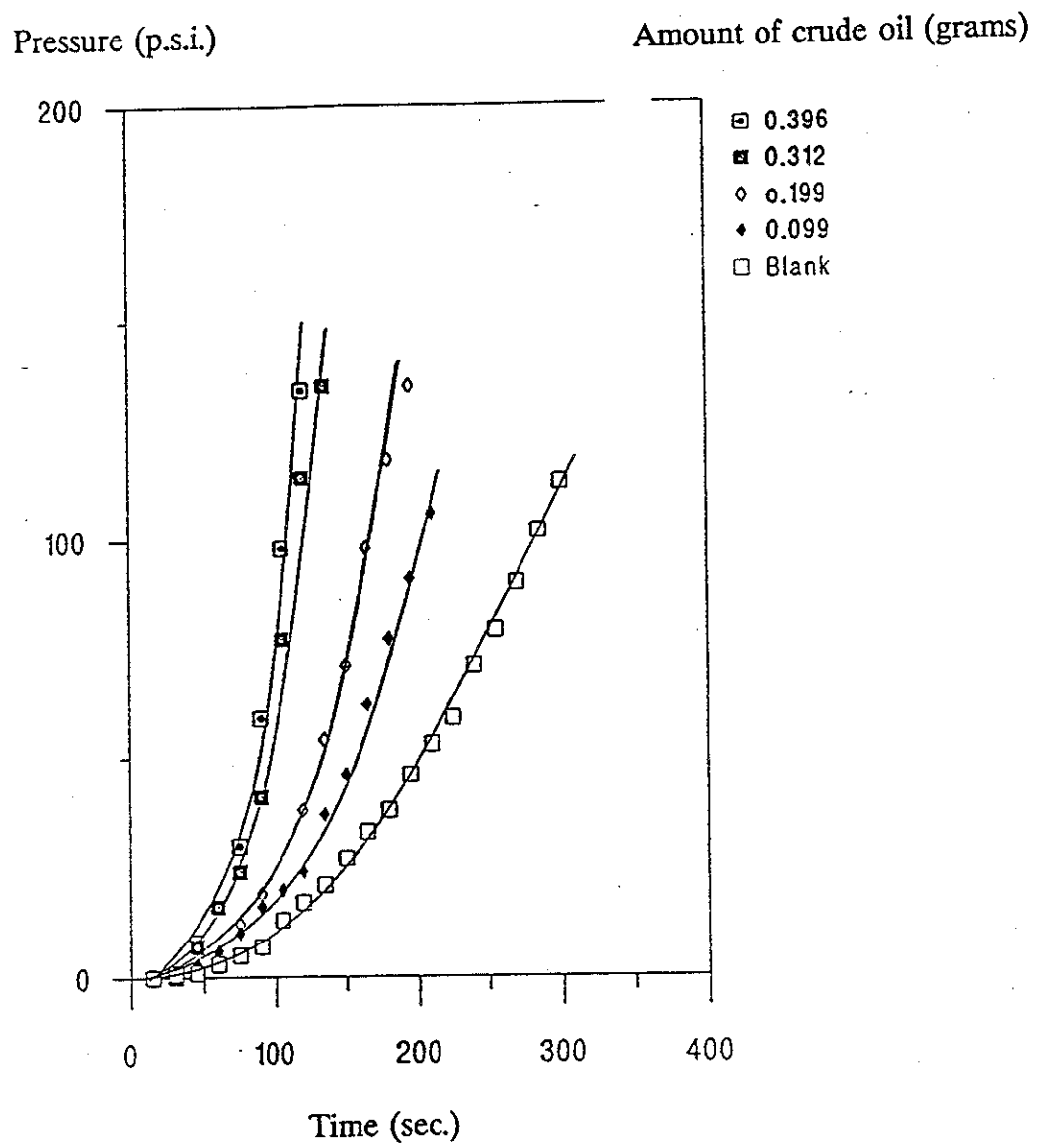◻ Blank

100

0

0　　100　　200　　300　　400

Time (sec.)

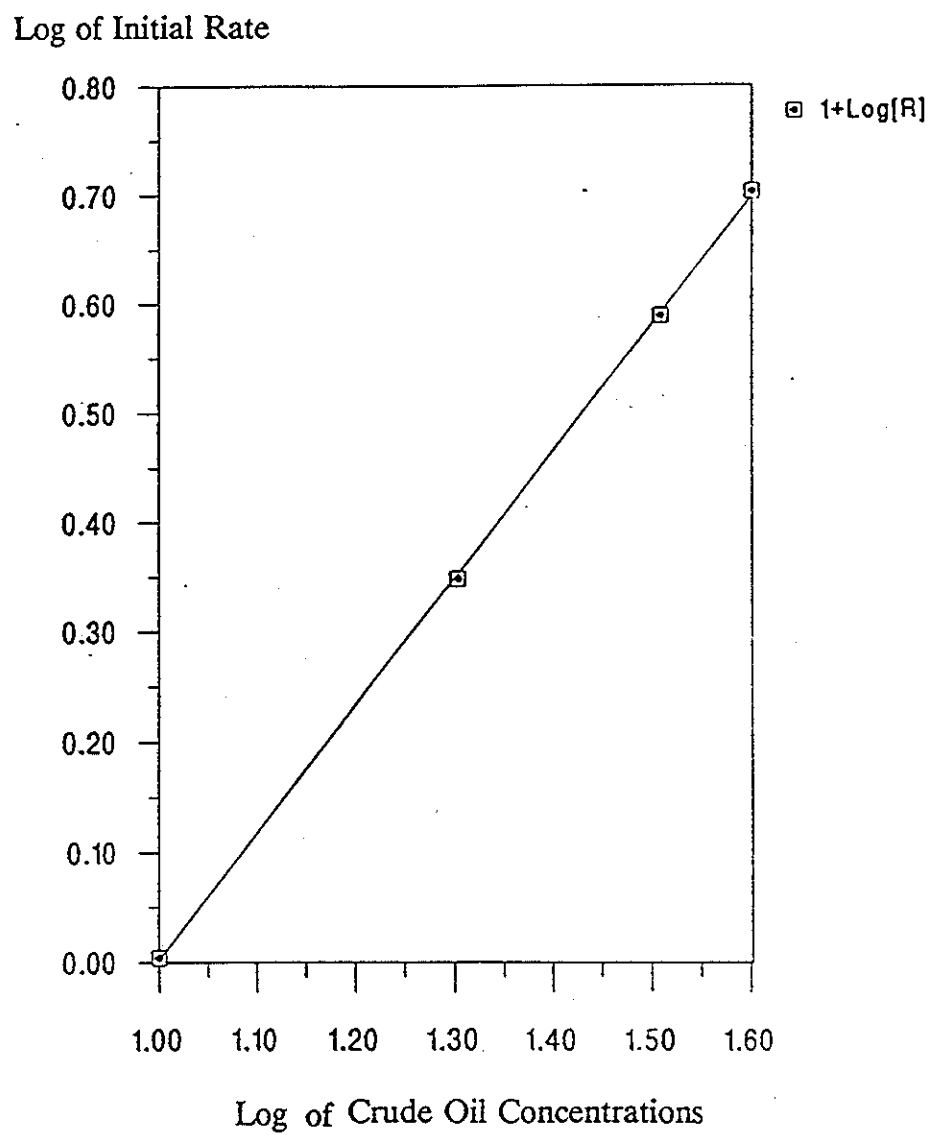Fig.3a　Pressure-time curves for varying amounts of Cold Lake crude oils

Fig.3b Initial Rate versus concentration of Crude Oil (shows first order dependence)

indicate that there is a strong linear relation between initial rates and log of the viscosities and between the log of initial rates and densities. These experimental results will be useful to design the conditions or parameters for microwave digestion of oils using their readily obtainable values of density or viscosity.

The mechanism of the microwave digestion processes for crude oil/nitric acid system is quite complicated. The different kinetic behaviour during the microwave digestion for different crude oil samples may indicate the dependence of the kinetics on the chemical composition of the crude oil. Table 1 shows the general trend that the aromatic hydrocarbons in crude oil increases with increasing density or viscosity. The dependence of the initial rate on the aromatic hydrocarbon content in different crude oils is shown in Figure 2c.

It has been noted by several investigators that the benzene ring is difficult to decompose with nitric acid under microwave digestion conditions.[11] The PTFE bomb microwave decomposition experiments (10-15 minutes at 180°C) also showed that o-, m-,and p-nitrobenzoic acid, small amount of dinitrobenzoic acid and several aromatic compounds remained in the reaction vessel. Experimental results of crude oil microwave digestion in this lab also show that the difficulty of crude oil digestion increases with increasing aromatic hydrocarbon content.

Figure 4a and 4b show the UV spectra of the solutions obtained from microwave digested crude oil/HNO$_3$ samples. These were diluted to 50 ml. The absorbency peaks observed between 300-400 nm are probably due to nitro-unsaturated hydrocarbons, nitro-aromatic compounds or nitro- polynuclear aromatic compounds. Similar spectra (Fig.4c) were obtained from the solutions of benzene, cyclohexene, cyclohexane and hexane in nitric

Absorbance (Relative)

Cold Lake

Alberta
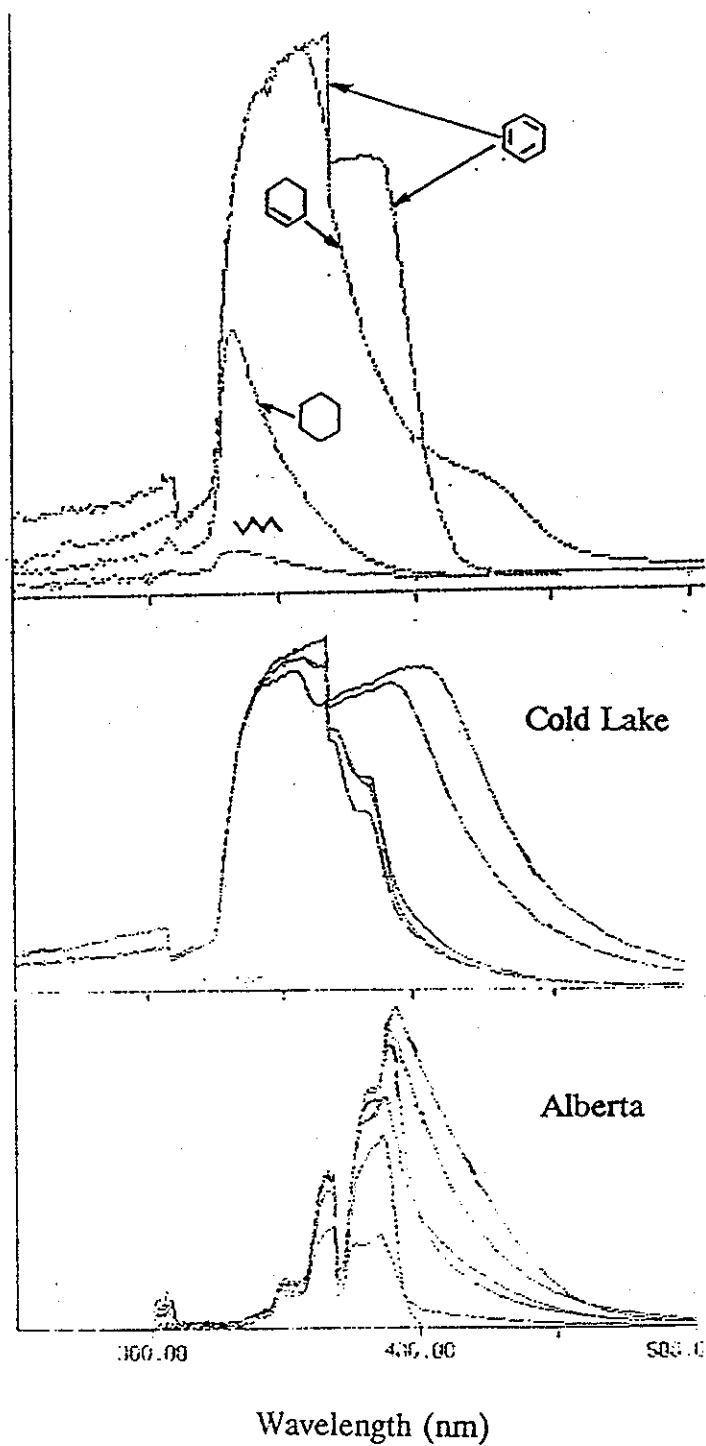
300.00　　　　　　400.00　　　　　　500.0

Wavelength (nm)

Fig.4 (a) UV spectra of microwave digested solutions of Alberta crude oil, (b) UV spectra of microwave digested solutions for Cold Lake crude oil; (c) UV spectra of Benzene, cyclohexene, cyclohexane and hexane in nitric acid.

Relative Absorbance

Oil type

☐ Cold Lake

☐ Alberta
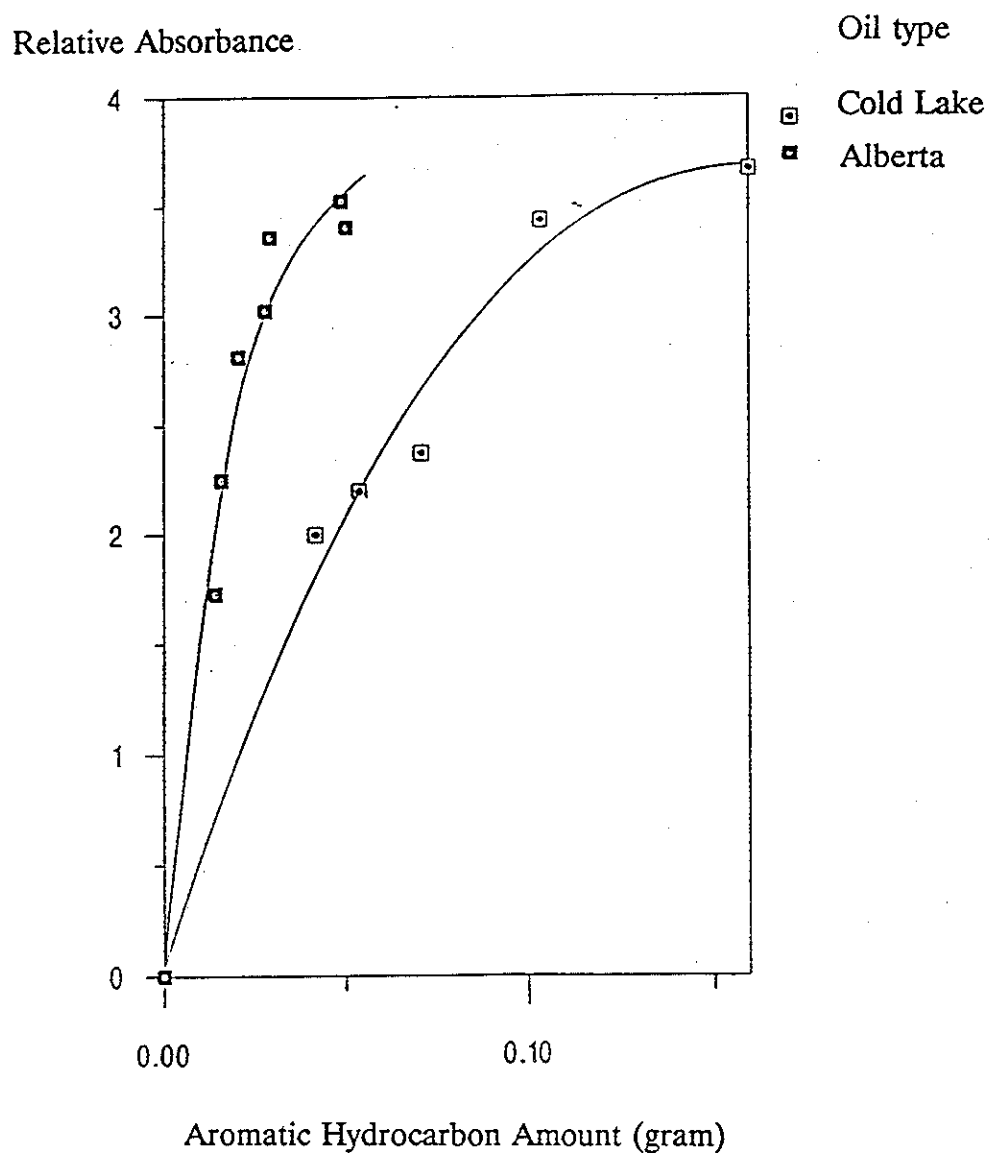

Aromatic Hydrocarbon Amount (gram)

Fig.5 Dependence of Absorbance on the Amount of Aromatic Hydrocarbon

acid, using nitric acid as reference. The differences in the UV spectra between ASMB crude oil samples and Cold Lake crude oil may indicate different nitro-hydrocarbon compounds which still remained after the microwave digestion process.

The correlation of UV absorbance and the amount of aromatic compounds, as shown in Fig. 5, indicates the general trend that residues of nitro-aromatic compounds or nitropolynuclear aromatic compounds in the digested solutions increase with increasing the content of aromatic hydrocarbons in oils.

2. Microwave digestion reactions of C_6 hydrocarbons with nitric acid

In order to better understand the mechanism of the oil microwave digestion the reactions between nitric acid and four typical C_6 hydrocarbons: benzene, cyclohexene, cyclohexane and hexane, have been studied in the microwave oven using the real time-pressure monitoring.

The reactions between C_6 hydrocarbons and nitric acid were studied under conditions similar to that for kinetic study on crude oil digestion. For each experiment, 10 ml concentrated nitric acid (70%) was used to react with different amount of C_6 hydrocarbons, ranging from 0.05 to 0.5 grams, at a microwave energy of 378 Watts.

Figure 6 shows the typical pressure-time curves for reactions between nitric acid and 0.2 grams of cyclohexene, cyclohexane, hexane and benzene, respectively. Figure 6 was plotted by subtraction of the blank (10 ml nitric acid) contribution to the pressure. Figure 6 clearly shows that the rates at the early stages are increased in the direction benzene, hexane, cyclohexane to cyclohexene. However, at the final stage, reaction rates seem to be the same. These results suggest that for microwave digestion of C_6 hydrocarbons, the
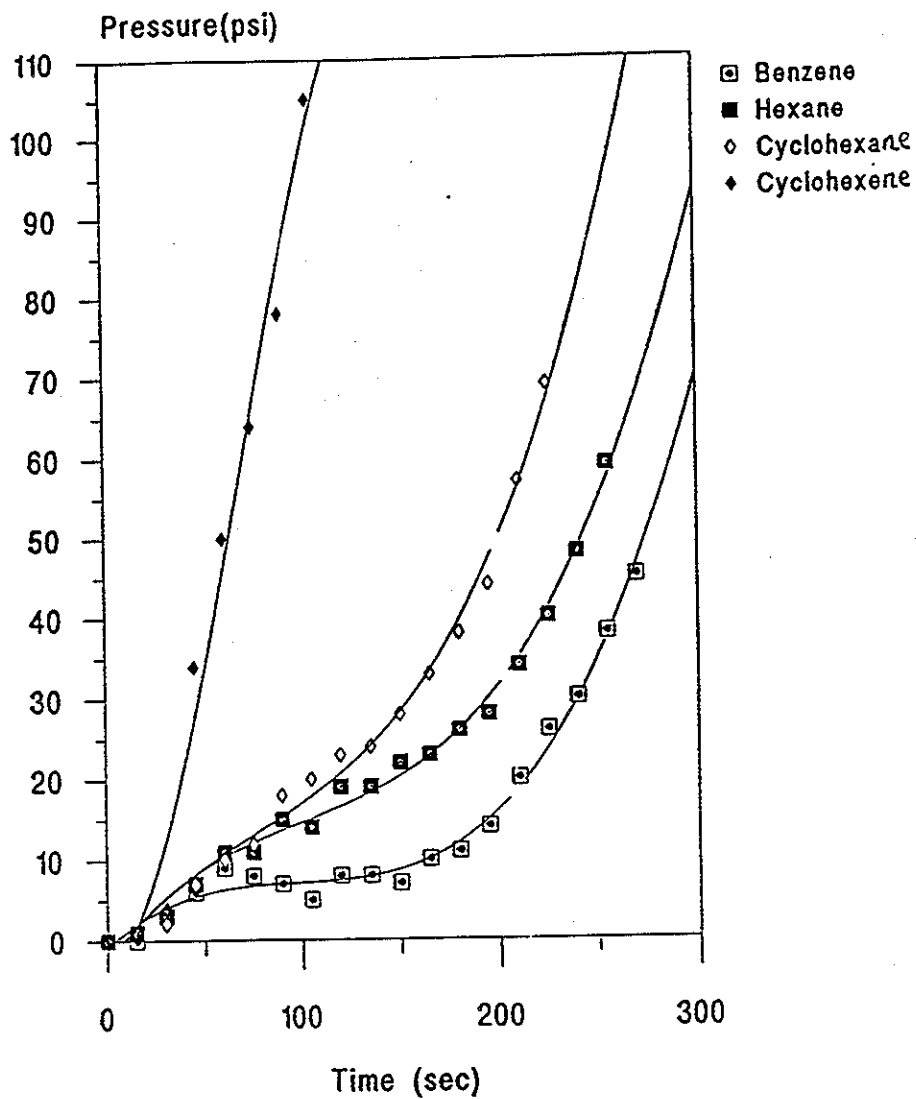
Figure 6. Pressure-Time curves for digestion of C_6 hydrocarbons with substraction of the contribution from the blank.

pressure control is particularly important at the early stages. After the early stages, the oxidation of various C_6 hydrocarbons by nitric acid in the high pressure vessel does not seem to be significantly different. The same results can be found from the microwave digestion of crude oils. The pressure-time curves look similar for different crude oils in the final stages of the reaction.

The reaction between cyclohexene and nitric acid was studied through real time-pressure monitoring with the data acquisition at one second intervals, as shown in Figure 7. Figure 7 indicates that after the initial induction period, there is a second stage, in which the pressure rises very quickly before entering the third reaction stage. Table 2 lists the kinetic data measured at these three stages using different amounts of cyclohexene. Figures 8a, 8b, and 8c show the reaction orders with respect to cyclohexene to be 1.16, 2.12 and 0.97 for the induction period, second stage and third stage respectively. The fact that the reaction order with respect to cyclohexene at second stage is much higher than that of the induction period and that of the third stage, may reflect that the second stage is most probably the chain propagation responsible for the radical reaction mechanism.

The reactions of cyclohexene with NO_2 both in gas phase and in liquid phase have been recently studied.[16-17] It was proposed that the radical addition mechanism (1) or the hydrogen abstraction mechanism (2) are responsible for the initial steps of the reaction between NO_2 and cyclohexene:

$$NO_2 \; + \; \bigcirc \; \text{-----}> \; \bigcirc\!\!-NO_2 \qquad (1)$$

$$NO_2 \; + \; \bigcirc \; \text{------}> \; \bigcirc\cdot \; + \; HONO \qquad (2)$$
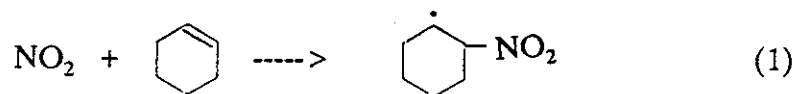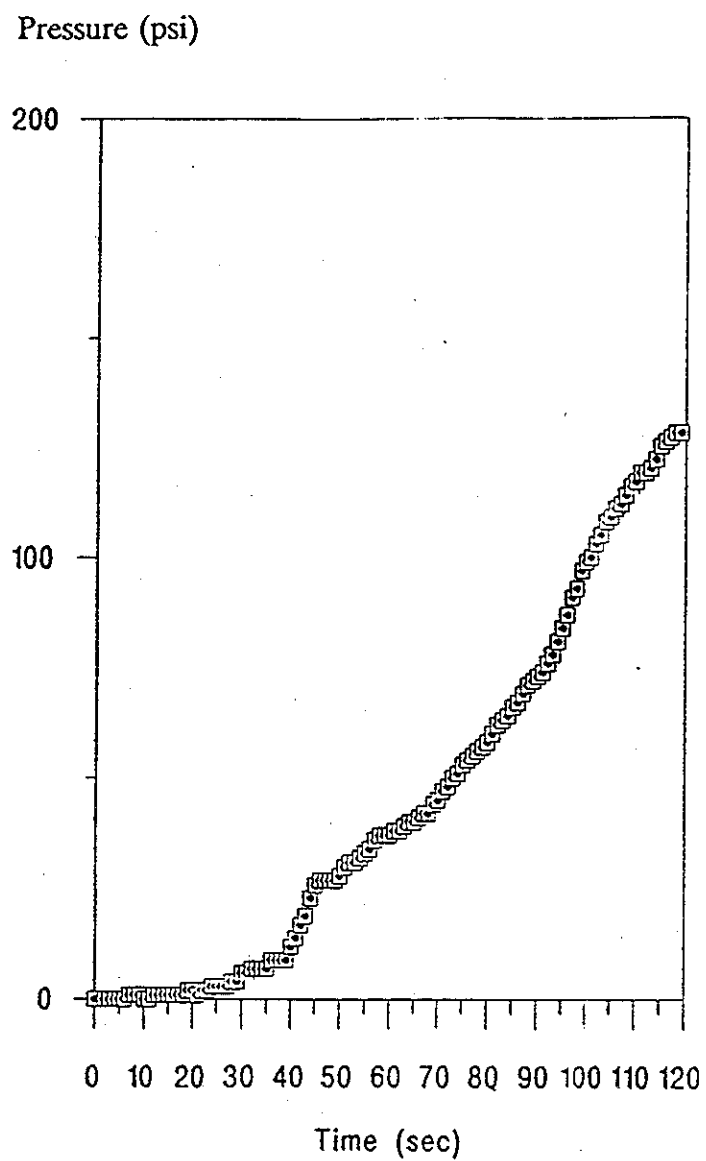
Pressure (psi)

Figure 7. Pressure-Time curve for reaction of cyclohexene (0.248 gram) with nitric acid (10 ml) at the microwave energy of 378 Watts.

Table 2. Kinetic data for the reaction of cyclohexene with nitric acid

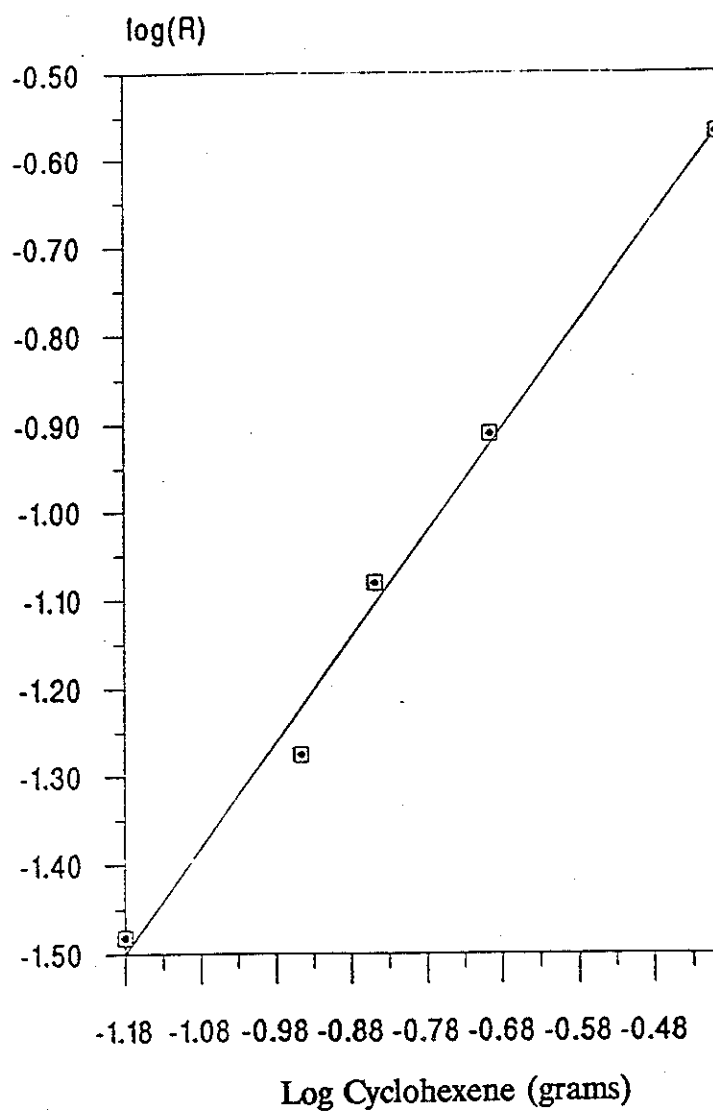| Cyclohexene (g)	Nitric Acid (ml)	Rate (psi/sec)		
		Stage (1)	Stage (2)	Stage (3)
0.066	10	0.0329	0.23	0.42
0.113	10	0.053	0.725	0.6
0.142	10	0.0829	1.05	0.7
0.202	10	0.123	2.25	1.12
0.248	10		2.9	1.5
0.401	10	0.27	14	

Figure 8a. Reaction order at first stage

Log Cyclohexene (grams)

Figure 8b. Reaction order at second stage

Log(R)
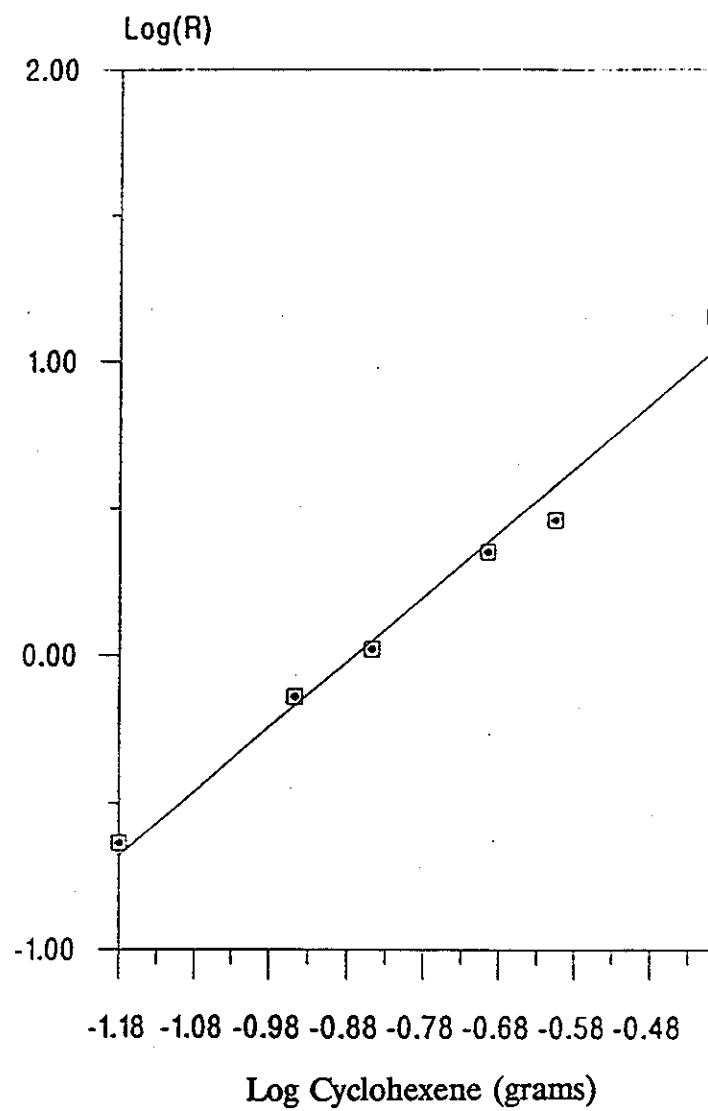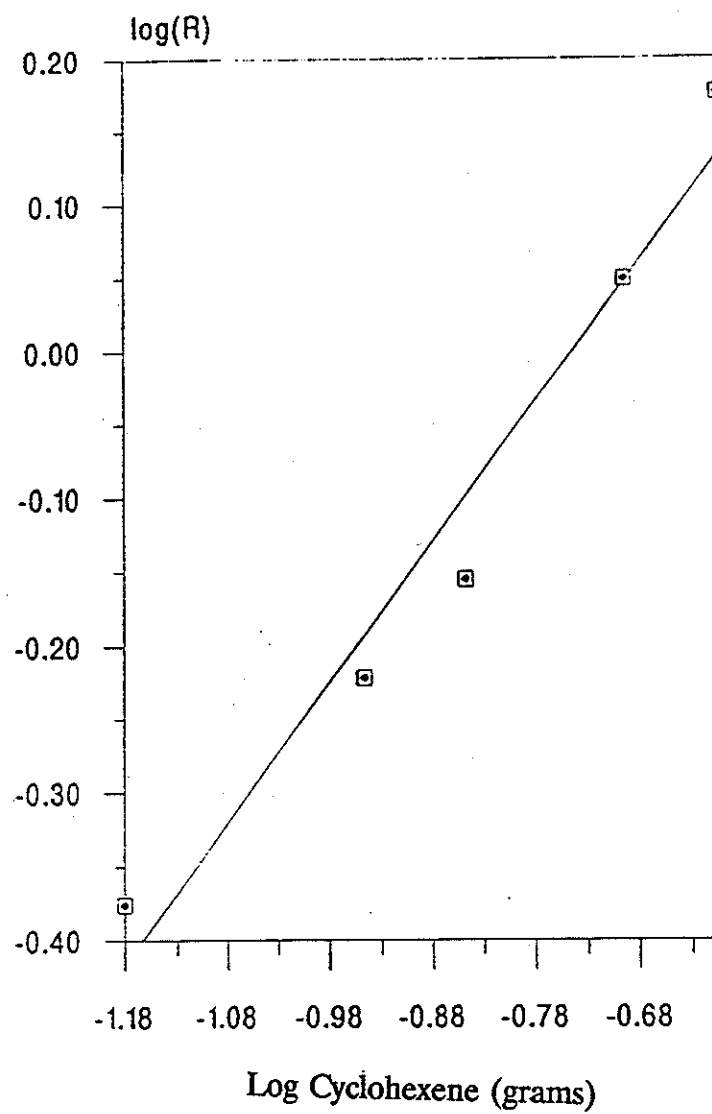
Log Cyclohexene (grams)

Figure 8c. Reaction order at third stage

Log Cyclohexene (grams)

The initial reaction orders were reported to be 1.2 with respect to cyclohexene and 1.8 with respect to NO_2.[17] The study of the reaction of cyclohexene with nitric acid under microwave conditions has not yet been reported. The reaction of cyclohexene with nitric acid in the closed vessel using microwave energy would be more complicated than the reaction of cyclohexene with NO_2. The radical mechanism of the reaction of cyclohexene with nitric acid and the measured reaction order of 1.16 (with respect to cyclohexene) may indicate its relation to the reactions of cyclohexene with NO_2.

The amount of gas phase products formed during the digestion of C_6 hydrocarbons by nitric acid can be monitored via the pressure in the reaction vessel. For the blank experiment, the closed vessel containing only 10 ml nitric acid (70%), equivalent to 0.155 mol of HNO_3, was heated at the microwave energy of 378 Watts with pressure at 135 psi for 20 minutes, then cooled down to room temperature. The final pressure reading (P_o) was 2 psi. This pressure is equivalent to 7.3×10^{-4} mol of gas phase products. Therefore, only less than 0.5% of HNO_3 decomposed during the microwave heating. Differing amount of C_6 hydrocarbons, ranging from 5×10^{-4} to 5×10^{-3} mol, were digested by 10 ml nitric acid with the same procedure as that of the blank experiment and the final pressure readings (P_s) were taken. It is assumed that the difference between P_s and P_o is due to the gas phase products formed during the digestion of C_6 hydrocarbons. Figure 9 is plotted using (P_s - P_o) versus the amount of C_6 hydrocarbons for digestion. The composition of the gas phase products formed during microwave digestion of C_6 hydrocarbons were examined using automobile emission analysis equipment. The major gas phase products are nitrogen oxides, NO_x, (50-60%) and carbon monoxide CO (25-30%), as shown in the Table 3. Figure 9 shows that the ratio of the yield of gas phase products to the amount of C_6 hydrocarbons

Yield
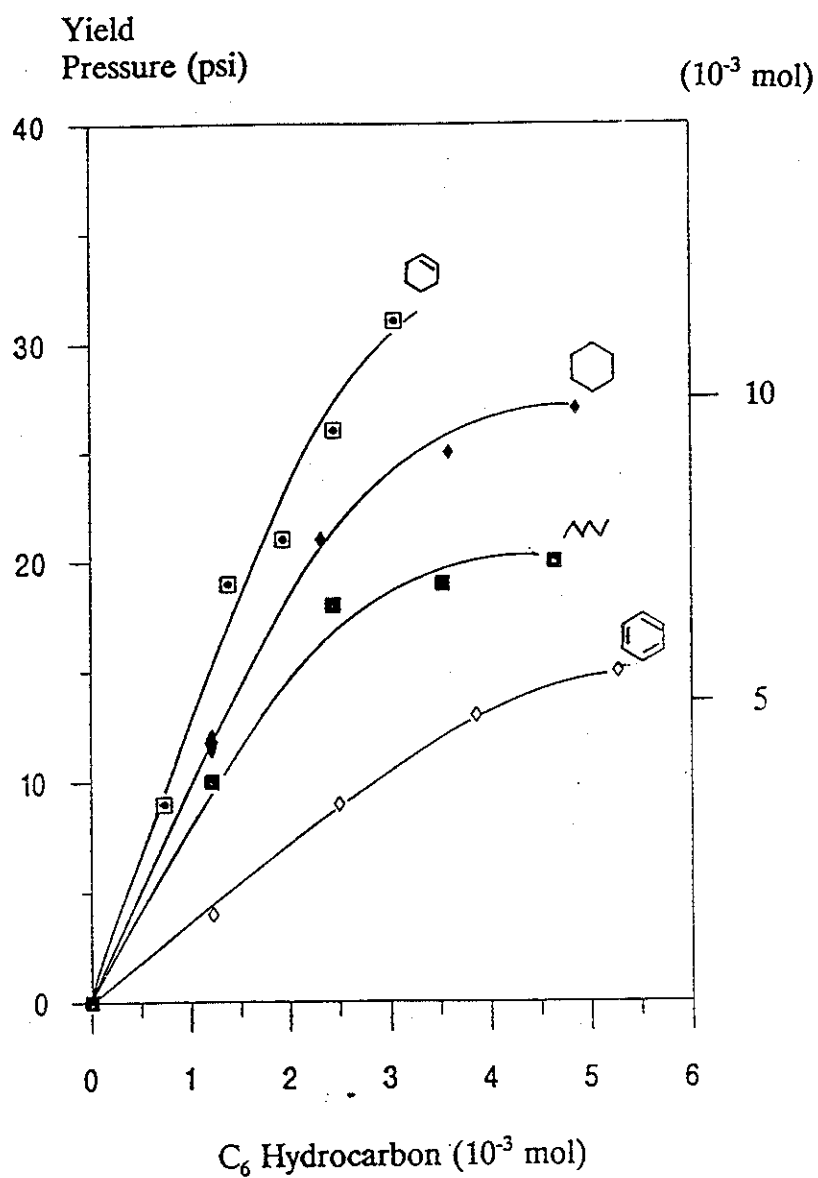Pressure (psi)   (10⁻³ mol)

Figure 9 Dependence of the yield of the gas phase products on the amount of C₆ hydrocarbons

Table 3. Gas phase products formed during microwave digestion of C6 hydrocarbons

C6 Hydrocarbons	(mol/1000)	Gas Phase Products (mol/1000)			
		NOx	CO	CO2	Hydrocarbon
Benzene	5.79	4.73	1.72	0.0014	0.134
Hexane	4.06	5.83	2.71	0.0012	0.18
Cyclohexane	4.72	7.41	3.65	0.0018	0.22
Cyclohexene	3.22	10.4	3.42	0.0021	0.21

decrease with increasing amount of C_6 hydrocarbons. Of these C_6 hydrocarbons, benzene is the most difficult one to digest to gas phase products, CO or CO_2. Therefore, most of the benzene must remain in the liquid phase in the form of intermediate oxidation products or nitro-aromatic compounds. These results agree with previous observations[11] and demonstrate that the crude oils containing more aromatic hydrocarbons would be more difficult to digest.

3. Recovery of metals and sulphur in oil samples by microwave digestion

We chose Cold Lake crude oil for recovery tests because having high density and high viscosity, it is the most difficult one to digest as indicated previously. Cold Lake crude oil microwave digestion was studied by varying the amount of samples, nitric acid, hydrogen peroxide, changing the pressure in the digestion vessel and the time at those pressures. The recoveries were measured by ICP-AES. Results are summarized in Table 4 and Figures 10-15.

The digested Cold Lake oil samples are uniform liquids with dark brown colour. All samples were diluted to 50 ml total volume with deionized water. During dilution of the digested sample, fibrous precipitates were immediately formed. The amount of precipitate depended on the amount of Cold Lake oil sample added. No precipitation was observed in case of using 0.1 gram of Cold Lake crude oil with 20 ml of nitric acid. For the experiments using 0.1 gram of Cold Lake crude oil with 10 ml nitric acid and digested at 135 or 190 psi for 30 minutes, the light yellow solutions obtained after dilution were still clear and the recoveries for Ni and V were close to 100%. For experiments using 0.47-0.50 gram of Cold Lake crude oil, large amounts of precipitates were formed and gradually aggregated after

Table 4   Recoveries of Ni and V from Cold Lake oil sample under different microwave digestion conditions

Sample Amount(g)	Nitric Acid(ml)	H2O2(g)	Digestion Pressure(psi)	Time(Min.)	Ni(ppm)	Recovery (%)	V(ppm)	Recovery (%)
0.111	10	0	135	30	68	100	190	100
0.111	10	0.111	135	30	63.5	93.4	165	86.8
0.122	10	0.201	135	30	65	95.6	165	86.8
0.128	10	0.351	135	30	62.9	92.5	162	85.3
0.137	10	0	135	30	62.4	91.8	169	88.9
0.18	10	0	135	30	61.1	89.9	161	84.7
0.264	10	0	135	30	60.6	89.1	170	89.5
0.47	10	0	135	30	60.7	89.3	169	88.9
0.486	10	0	135	5	58.6	86.2	160	84.1
0.473	10	0	135	10	59.5	87.5	167	87.9
0.485	10	0	135	59	58	85.3	166	87.3
0.155	10	0	135	30	62	91.2	164.5	86.6
0.161	5	0	135	30	67.4	99.1	189	99.5
0.495	10	0	190	0.5	53.7	79	136	71.6
0.492	10	0	190	5	58.8	86.5	162	85.3
0.489	10	0	190	30	61.3	90.1	167	87.9

*Cold Lake Crude Oil: Density 1.00 (20C), Dynamic Viscosity 235000 c.p.(15C)
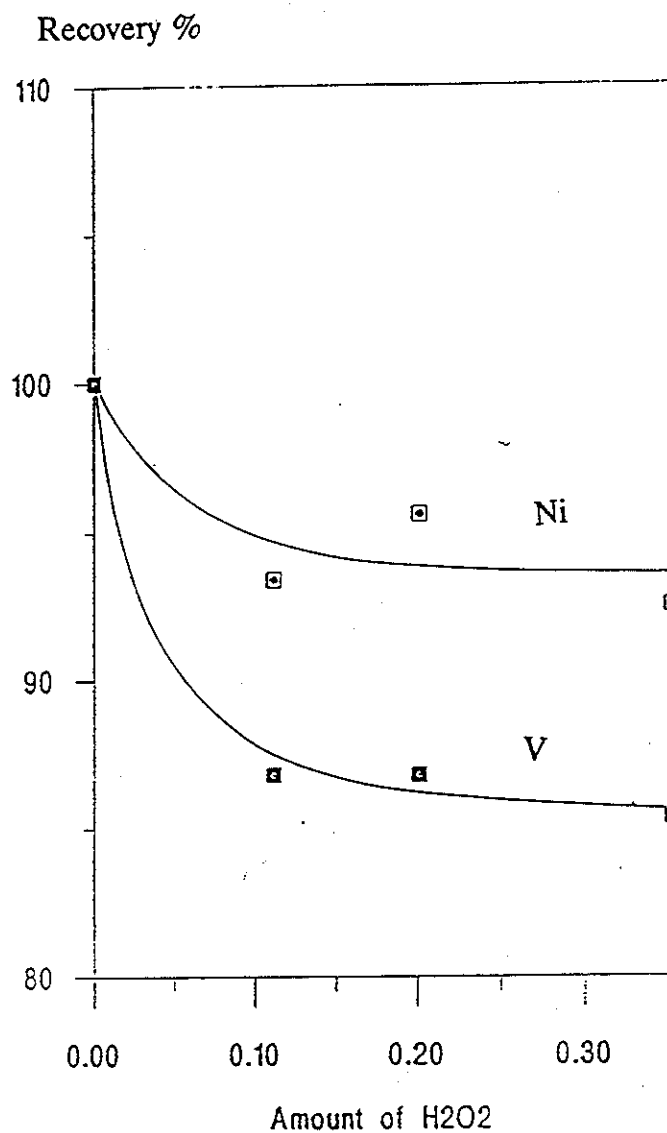
Figure 10. Effect of the amount of H_2O_2 (g) on the recovery of Ni ◉ and V ◘ .
Amount of Cold Lake crude oil sample 0.11-0.13 g, nitric acid 10 ml, microwave
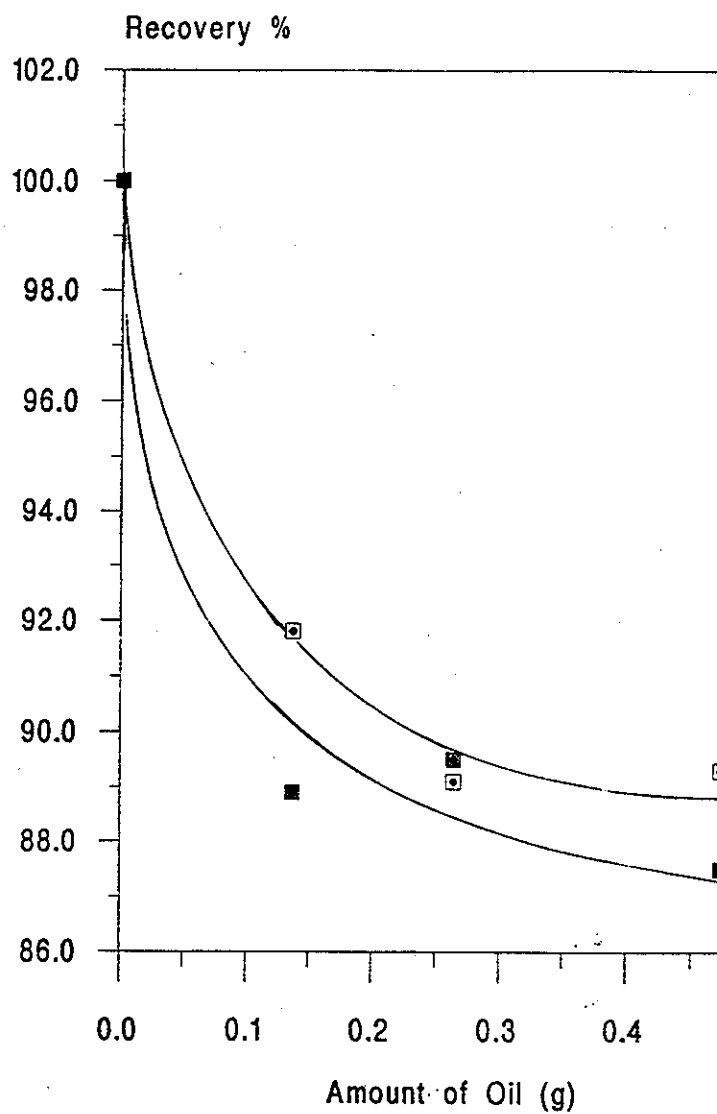digestion pressure 135 psi, time under pressure 30 minutes.

Figure 11. Dependence of recovery (Ni ▣ ,V ◪) on the amount of Cold Lake oil sample (g). Microwave digestion pressure 135 psi, time under pressure 30 minutes, nitric acid 10 ml.
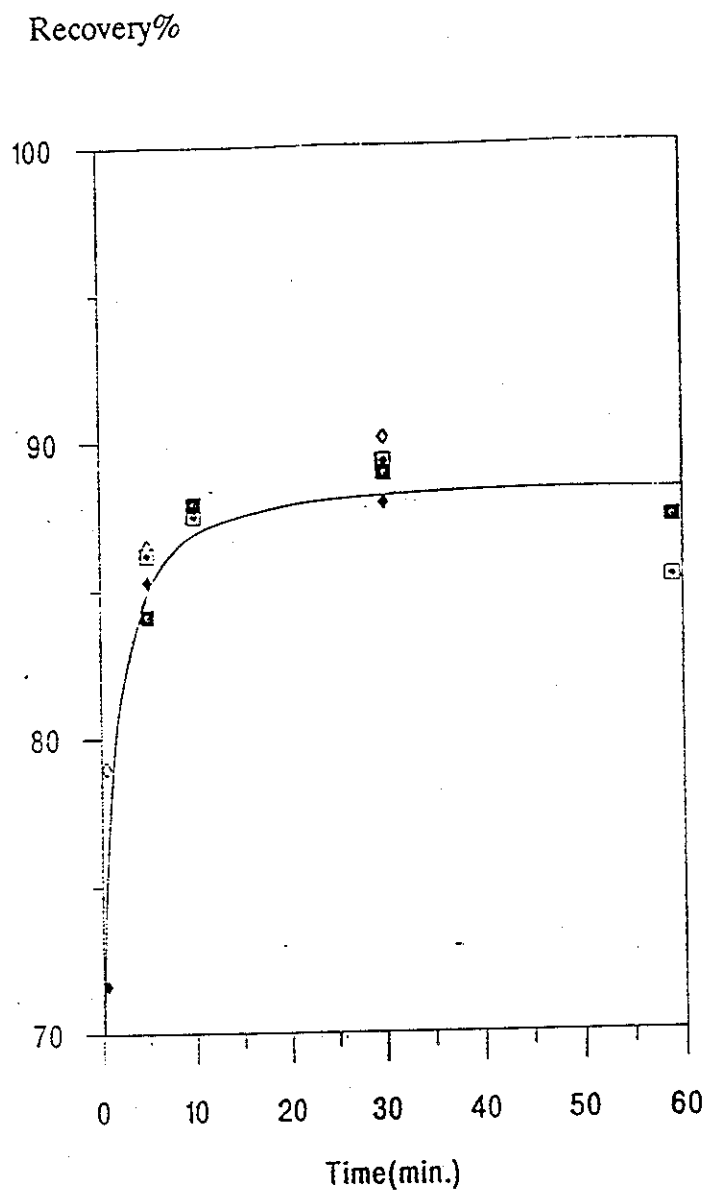
Recovery%

Figure 12. Dependence of recovery on the time under pressure: ⊡ Ni, 135 psi; ◪ V,135 psi; ◇ Ni, 190 psi; ◆ V,190 psi. Cold Lake oil sample 0.47-0.50 g, Nitric acid 10 ml.

Recovery %

Figure 13   Dependence of the sulphur recovery on the amount of Cold Lake oil sample.
Microwave digestion conditions: closed vessel pressure 190 psi for 30 minutes,
Nitric acid (70%) 10 ml.

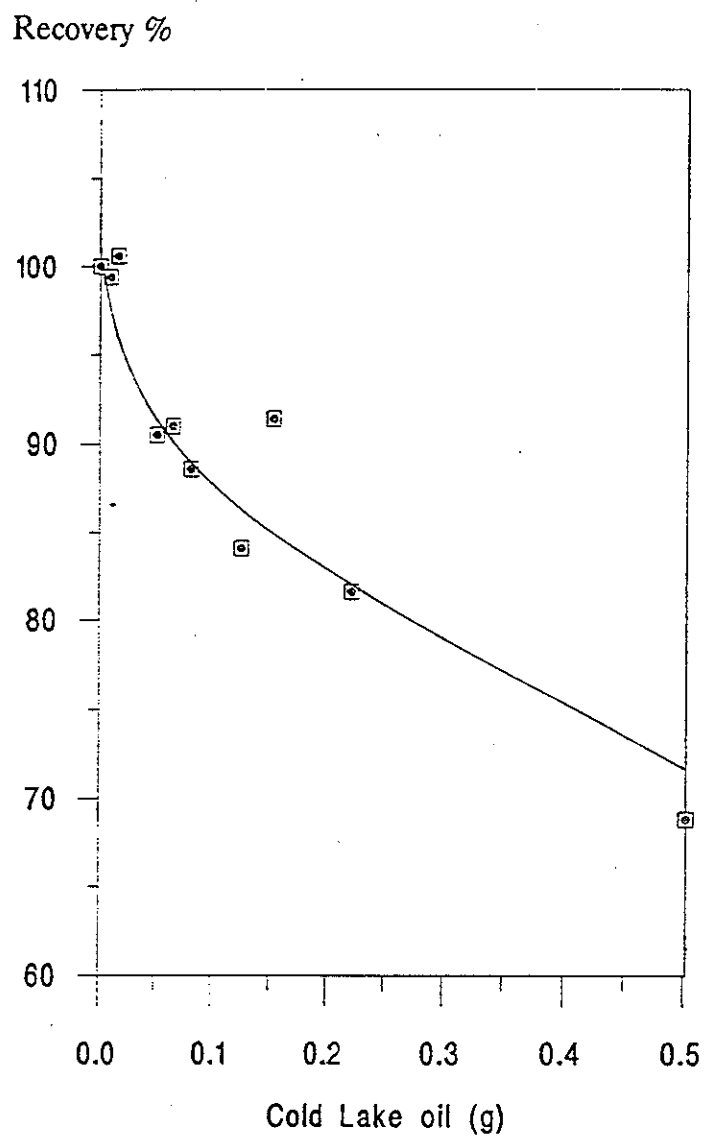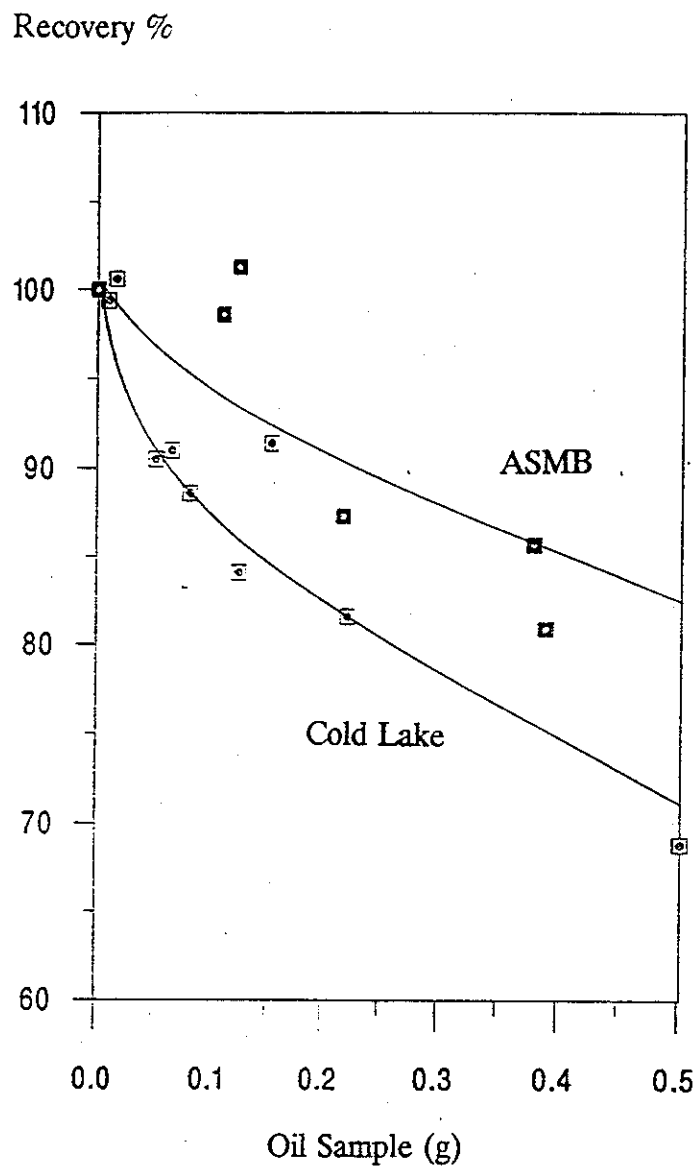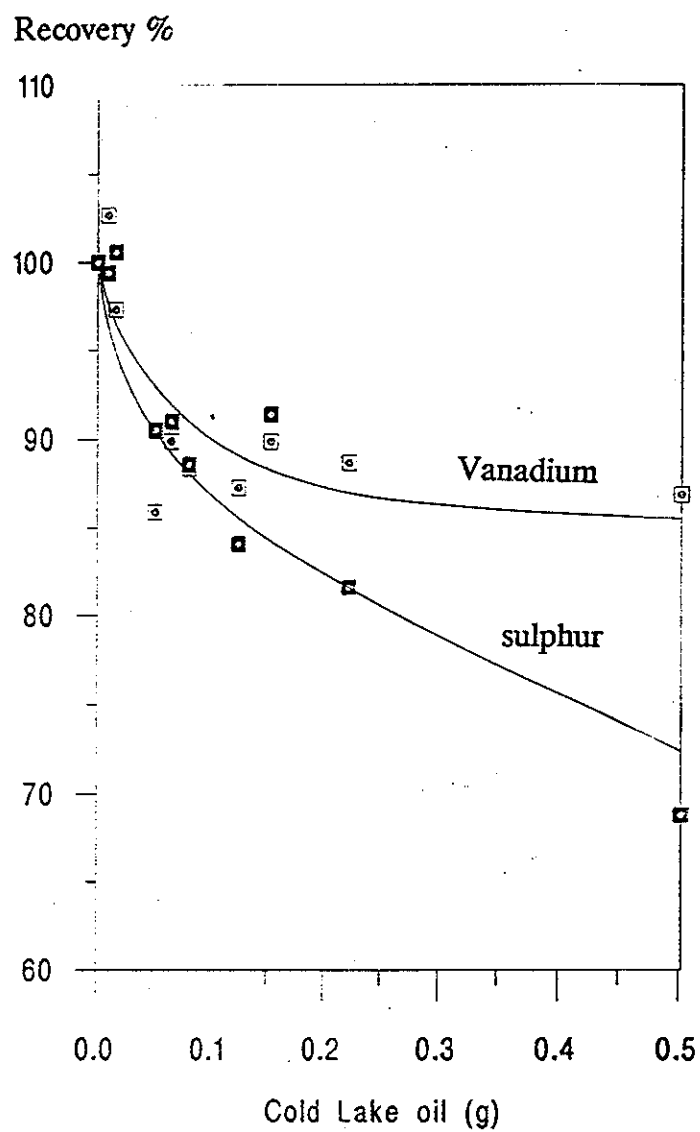Figure 14 Recovery of sulphur for Cold Lake oil and ASMB oil at same microwave digestion conditions.

Figure 15 Comparison of sulphur recovery with Vanadium recovery at same microwave digestion conditions.

several days. Centrifuge could not effectively separate the newly-formed fibrous precipitates, some of which were still suspended on the top of solution even after centrifuging at high speed (8500 rmp) for 15 minutes. The recoveries of Ni and V for those experiments using 0.5 gram of Cold Lake oils were 85-90%, as shown in Figure 12, and would not depend on the digestion time (if t>5 minutes) and pressures (135 psi or 190 psi). This may be explained by the formation of the precipitate, which could cause co-precipitation of metal ions and possibly cause adsorption of metal ions from the liquid phase to the solid surface.

Hydrogen peroxide was added to the Cold Lake oil samples to try to improve digestion and to prevent the formation of precipitates. Results in Table 5 and Figure 10 show that H_2O_2 does not affect the formation of precipitates and does not help recovery rates. The amount of nitric acid compared to the amount of the crude oils is the key factor which affects the formation of precipitates or the extent of digestion.

The studies on the recovery of sulphur in oils were carried out under similar microwave digestion conditions. The gas phase sulphur compounds which could be formed during the microwave digestion of the Cold Lake oil samples were checked by absorbtion into solution, then measurement by ICP-AES. Results indicate that less than 1 percent of sulphur content in the original oil sample was transferred into gas phase products. The recovery of sulphur is strongly dependent on the amount of oil sample to be digested. Figure 13 shows that the sulphur recovery decreases with increasing oil amount. For higher-sulphur-content samples (Cold Lake oil) the recovery declines faster than that of lower sulphur content sample (ASMB), as shown in Figure 14. For the same oil (Cold Lake oil) at the same microwave digestion conditions, the recovery of sulphur is much lower than the

Table 5. Microwave digestion of Cold Lake oil

Sample(g)	Nitric acid(ml)	Hydrogen Peroxide(g)	Color	Precipitation
0.111	10	0	light brown	yes
0.111	10	0.11	light brown	yes
0.122	10	0.2	light brown	yes
0.107	10	0.33	light brown	yes
0.128	10	0.35	light brown	yes
0.103	20	0	light brown	no

Table 6. Sulphur content in oil samples

No.	Sample	Sulphur (wt%) by ICP	Sulphur (wt%) from Catalogue	
1	Bent Horn A02	0.749	0.76	
2	West Texas Sour	2.05	1.9	
3	Hibernia Fv16%	1.09	0.65	(0% weathered)
4	Lago medio	0.967	1.23	
5	ASMB	0.566	0.55	
6	Ninian crude	0.347	0.41	
7	Ninian Fv 15.2	0.43		
8	Panuke	0.014	0.04	(0% weathered)
			0.02	(32.1% weathered)
			0.04	(47.4% weathered)
			0.02	(53.2% weathered)
9	Synthetic crude	0.136	0.23	(0% weathered)
			0.15	(11% weathered)
			0.20	(22.4% weathered)
10	Adgo	0.122	0.19	
11	Atkinsion	1.1	0.86	
12	Avalon s-34	0.87		
	Avalon		0.71	
13	Aviation gas 100	0.022	<0.05	
14	BCF-24	2.43	3.85	
15	Insulating oil	0.09	0.08	
16	Endicot	0.835	1.34	
17	Marine Intermediate	2.19	2.7	
18	Maya	3.52	3.4	
19	California API 11	3.25	3.3	
20	Oseberg	0.32	0.31	
21	Bent Horn Fv20.6	0.98	0.82	(0% weathered)
22	Terra Nova	0.415		
23	Sumatran Duri	0.244		
24	Berlidge	1.28		
25	Platform Irene	3.61		
26	FCC Heavy Cycle Fv9%	0.121		
27	Normal well	0.233		
28	Irenian Heavy crude	1.76		
29	Port Hueneme Fv14%	4.76		
30	FCC/VGO	0.0026		
31	Home Furnace oil	0.169		
32	Hondo Fv16.7%	5.61		
33	Sockeye	3.43		
34	North slope w20.2%	1.75		
35	Nerlerk Fv15.98%	0.279		
36	Nektorlic Fv9.9%	0.213		
37	Santa Clara	3.88		

38	Taching Crude	0.109
39	Arabian light Fv24%	1.91
40	West Texas Intermediate	0.478
41	Hog oil	1.32
42	Udang crude	1.11
43	Carpenteria Fv10.3%	2.34
44	Hugh Brown Dilunt	0.11
45	Trasoil #10AEC	3.63
46	Cat. Cracking Feed Fv2%	0.337
47	Waxy light	1.06
48	Pitas point	0.55
49	Niguinian	0.054
50	Sumatran light minas	0.091

recovery of vanadium, as indicated in Figure 15. More than 50 oil samples have been tested sulphur using microwave digestion-ICP techniques. The results reported in Table 6 have been corrected for the recovery, based on sample quantity. Table 6 also presents data on the sulphur content of 20 oils from the oil properties catalogue[18] for comparison with present ICP measurements. The general agreement of ICP methods with previously reported results, is encouraging.

Conclusions

The Pressure-Time curves monitored during oil microwave digestion in closed vessels reflect the kinetics and mechanisms of the microwave digestion process. The studies on the mechanism of C_6 hydrocarbon digestion show that pressure control in the early digestion stages is particularly important. The first order dependence of the initial rate on the amount of oil sample and the relation of the initial rates with densities, viscosities and hydrocarbon compositions are useful for predicting the pressure control. The difficulty of oil digestion increases with increasing aromatic hydrocarbon content. The recoveries of metals and sulphur depended on two main factors: the digestion or oxidation extent and the amount of the precipitates formed. Both of these two factors are related to the hydrocarbon composition of the oils and the amount of oil to be digested. The recoveries, in general, increase with decreasing the oil amount. However, the sensitivity for trace metal detection in oil decreases with decreasing the oil sample amount. For the better results and safer operations, the high pressure microwave digestion of oil samples should be grouped in several categories according to oil densities, viscosities and hydrocarbon compositions. The

Table 7. Oil sample category designation

Category	Density (15C)	Viscosity (c.p. at 15C)	Aromatic Hydrocarbon (%)
A	<0.83	<4	<12
B	0.83 - 0.88	4 – 40	12 – 16
C	0.88 - 0.92	40 - 100	16 - 20
D	0.92 - 0.97	100 - 6000	20 - 28
E	>0.97	>6000	>28

Table 8. Microwave digestion conditions for oil samples

Category	Oil Sample (g)	Nitric Acid (ml)	Microwave Power(W)	Pressure (psi)	Time (min.)
A	0.4	10	378	135	30
B	0.3	10	378	135	30
C	0.2	10	378	190	30
D	0.15	10	378	190	30
E	0.1	10	378	190	30

Table 9. Concentrations (in ppm) of 12 elements in oil samples

No.	Sample	Mo	P	Zn	Pb	Ni	Fe	Cr	Mg	V	Cu	Ti	Ba
1	ASMB	0.6	<1.5	<0.6	<3	2	<3	<1.5	1.2	14	0.6	<0.6	0.6
2	ASMB15%	0.6	3.2	0.6	3	3.2	<3	<1.5	1.7	18.4	<0.6	0.6	0.3
3	ASMB22.8%	<0.6	<1.5	0.9	<3	3.3	34	<1.5	2.4	21.4	<0.6	<0.6	0.3
4	ASMB25%	1	6	5.3	3	4.5	69	<1.5	3.7	24.3	5	<0.6	0.7
5	Calif.API15	5.1	<1.5	<0.6	3	111	9.1	1.7	8	266	<0.6	2.2	1
6	Calih.API11	4	<1.5	<0.6	3	106	21.5	1.5	237	245	<0.6	2.2	1
7	BetaCrude	<0.6	<1.5	<0.6	<3	112	68	<1.5	25	146	<0.6	2.2	1.4
8	Canola oil	<0.6	<1.5	<0.6	<3	<1	<3	<1.5	28	<0.6	<0.6	<0.6	<0.3
9	Avalon s-34	0.8	1.9	<0.6	<3	2.1	13	<1.5	4.4	1.6	1.1	<0.6	4.9
10	Avalon B27	2.2	<1.5	<0.6	<3	<1	5	<1.5	4.7	<0.6	<0.6	<0.6	1.8
11	A Medium crude	0.6	1.6	1.6	4.8	9.5	6.8	2.6	14.5	46	1.6	<0.6	0.3
12	Arabian light	0.9	<1.5	<0.6	<3	2.5	<3	<1.5	5.6	16	1.6	<0.6	<0.3
13	Arabian light Fv24.2	<0.6	<1.5	5.1	3.9	3.3	6.3	<1.5	2.7	19.6	2.4	<0.6	0.4
14	Cohesset	0.9	7.2	2.6	9.4	<1	24.3	3.9	26.9	1.9	8.5	2	1.3
15	Atkinson	0.6	2	1.4	3.5	1.8	6.7	<1.5	4.6	9.4	<0.6	0.6	0.6
16	Atkinson19.4%	<0.6	2	2.6	3.7	2.7	66	<1.5	4.5	11	0.6	<0.6	0.6
17	Bent Horn Impr.Tan	<0.6	<1.5	<0.6	<3	<1	56	<1.5	3.4	<0.6	<0.6	<0.6	<0.3
18	Bent Horn20.4%	1.3	2	3.9	<3	<1	70	<1.5	24	<0.6	2.3	0.6	1
19	Bent Horn20.6%	0.9	<1.5	1.9	<3	<1	19	<1.5	16	<0.6	<0.6	<0.6	0.6
20	Bent HornA02	<0.6	<1.5	2.9	<3	6.5	8.4	<1.5	36.6	<0.6	<0.6	<0.6	1.9
21	Aviation Gas100	<0.6	<1.5	<0.6	795	<1	<3	1.4	7.5	<0.6	<0.6	<0.6	<0.3
22	AviationGas80	0.6	<1.5	<0.6	175	<1	<3	<1.5	8.2	<0.6	1.1	<0.6	<0.3
23	AdgoFv34	1.1	<1.5	1.4	<3	1.9	51	3.1	42	<0.6	1.4	2.2	2.5
24	Adgo fresh	<0.6	<1.5	1.4	<3	<1.2	47	<1.5	16.5	<0.6	<0.6	<0.6	18.9
25	JP-4 NATO F40	<0.6	<1.5	<0.6	<3	<1	<3	<1.5	3.8	<0.6	<0.6	<0.6	<0.3
26	Jet A-1	1.9	<1.5	2.4	<3	<1	39	<1.5	9.6	<0.6	<0.6	2.7	0.3
27	Jet A-1 Fv45.5	<0.6	<1.5	0.8	<3	<1	<4	<1.5	4.7	<0.6	<0.6	<0.6	<0.3
28	Jet-B Fv32	<0.6	<1.5	0.6	<3	<1	13	<1.5	3.6	<0.6	<0.6	<0.6	<0.3
29	Cat Cracking Feed	<0.6	<1.5	0.9	<3	1.8	<3	<1.5	3.7	<0.6	<0.6	<0.6	<0.3
30	Cat Cracking Fv2.06	<0.6	<1.5	0.6	<3	4.7	4.5	<1.5	8.7	0.6	<0.6	<0.6	0.4
31	Boscan Crude	4.7	1.8	4.7	<3	117	56	<1.5	16.3	1320	1.6	<0.6	0.5
32	Carpenteria	<0.6	<1.5	<0.6	<3	48.9	29.5	<1.5	<1	112	<0.6	<0.6	<0.3
33	Carpenteria Fv10.3	1.3	<1.5	0.9	<4	58.4	32.4	<1.5	4.1	112	<0.6	0.9	<0.3
34	Carpenteria Fv14.9	<0.6	<1.5	<0.6	<3	65.5	35.9	<1.5	1.4	148	<0.6	<0.6	<0.3
35	Cold Lake	3.7	<1.5	4.3	<3	69	15.2	<1.5	9	190	<0.6	<0.6	<0.3
36	Bunker C Fuel	<0.6	<1.5	1.6	<3	8.6	35	<1.5	23.9	42	1.2	<0.6	<0.3
37	Bunker C light	0.9	<1.5	<0.6	<3	31	12.4	<1.5	4.7	157	<0.6	<0.6	<0.3
38	BCF 24	<0.6	<1.5	<0.6	<3	30	<4	<1.5	6.5	290	<0.6	<0.6	<0.3
39	BCF24 Fv9.23	<0.6	<1.5	<0.6	<3	23.6	5.2	<1.5	<1	248	<0.6	<0.6	<0.3
40	Belridge Heavy	<0.6	<1.5	<0.6	<3	70	40.4	<1.5	5.4	86.4	<0.6	<0.6	0.3
41	Diesel	<0.6	2.8	1.2	<3	<1	4.6	<1.5	12.3	<0.6	<0.6	<0.6	<0.3
42	Dos Cudra	<0.6	<1.5	<0.6	<3	62	42.1	<1.5	16	70.5	<0.6	<0.6	<0.3
43	Dos Cudra Fv11.7	<0.6	<1.5	<0.6	<3	51	42.3	<1.5	1.8	63.9	<0.6	<0.6	<0.3

#	Name												
44	Dos Cudra Fv20.3	<0.6	<1.5	0.9	<3	61	46.5	<1.5	7.4	74	<0.6	0.7	<0.3
45	Endicot	1	<1.5	<0.6	<3	5.4	<4	<1.5	<0.6	17.1	<0.6	<0.6	<0.3
46	Endicot 12.5%	<0.6	<1.5	<0.6	<3	5.2	<4	<1.5	0.6	18.4	<0.6	0.6	<0.3
47	Empire Crude	<0.6	<1.5	<0.6	<3	<1.5	39.5	<1.5	17.4	<0.6	<0.6	1.5	0.3
48	Extr.Pres.Gear oil	<0.6	10.1	488	<3	<1	<4	<1.5	235	0.6	11.4	<0.6	22.4
49	FCC Heavy Cycle	<0.6	<1.5	0.4	<3	<1	<4	<1.5	3.8	<0.6	<0.6	<0.6	<0.3
50	FCC Hvy Cyc Fv9.15	<0.6	<1.5	<0.6	<3	<1	<3	<1.5	<1	<0.6	<0.6	<0.6	<0.3
51	FCC/VGO	<0.6	<1.5	0.6	<3	<1	3	<1.5	6.5	<0.6	<0.6	<0.6	<0.3
52	Federated Crude	<0.6	<1.5	0.4	<3	<1	40.2	<1.5	11.8	1.3	<0.6	<0.6	<0.3
53	Heavy Reformate	<0.6	<1.5	<0.6	<4	<1	<4	<1.5	10.6	<0.6	<0.6	1.2	<0.3
54	Hondo Crude	2.3	<1.5	0.5	<4	75	30.5	<1.5	5.4	196	<0.6	1.6	0.3
55	Hondo Fv16.6	<0.6	<1.5	<0.6	<3	80.4	3.3	2.3	5.6	218	0.7	2	0.3
56	Hondo Fv32.2	0.6	<1.5	<0.6	<3	88	3	<1.5	9.1	228	1.5	2	0.3
57	Home Furnace	<0.6	<1.5	<0.6	<3	<1	<3	<1.5	0.5	<0.6	<0.6	<0.6	<0.3
58	Hog oil	<0.6	<1.5	2.4	<4	31	24.5	2	17	22.8	4.4	3.1	0.7
59	Hybernia Crude 16%	<0.6	<1.5	<0.6	<3	3.3	<3	2	11.4	3.5	<0.6	<0.6	0.3
60	Insulating oil new	0.8	<1.5	<0.6	<4	<1	92.4	<1.5	6.7	<0.6	<0.6	<0.6	0.3
61	Insulating oil used	<0.6	<1.5	2.4	<4	<1	32	<1.5	8.7	<0.6	<0.6	<0.6	<0.3
62	Iranian Heavy	<0.6	<1.5	<0.6	<3	22.6	6	<1.5	8.8	81	0.6	<0.6	<0.3
63	Lago medio	<0.6	<1.5	<0.6	<3	5.6	<3	<1.5	3.8	163	<0.6	<0.6	<0.3
64	Mayan Crude	1.2	<1.5	<0.6	<3	45.5	<3	<1.5	16.7	257	<0.6	<0.6	<0.3
65	Marine Intermediate	<0.6	<1.5	1.1	<3	29.5	29.5	<1.5	10.2	76.4	<0.6	0.6	1.4
66	Nektoralic Fv9.9	<0.6	<1.5	<0.6	<3	<1	<3	<1.5	3.9	0.7	1	<0.6	0.3
67	Nerlerk Fv15.9	<0.6	<1.5	4.5	6.2	<1	29.5	<1.5	3	<0.6	1.3	<0.6	8.6
68	Ninian crude	<0.6	<1.5	<0.6	<3	<1	4.2	<1.5	<1	4	<0.6	<0.6	<0.3
69	Ninian Fv15.2	<0.6	<1.5	<0.6	<3	<1	4.9	<1.5	<1	4.9	<0.6	0.5	<0.3
70	Ninian Fv30.2	<0.6	<1.5	<0.6	<3	1.3	6.6	<1.5	<1	6.4	<0.6	<0.6	<0.3
71	Norman Wells	<0.6	<1.5	<0.6	<3	3.3	<3	<1.5	<1	8.7	<0.6	<0.6	<0.3
72	North slope	<0.6	<1.5	<0.6	<3	7.2	7.8	<1.5	10.5	21.2	<0.6	<0.6	<0.3
73	North slope Fv20.2	<0.6	<1.5	<0.6	<3	14.7	14.2	1.9	1.6	33.9	<0.6	<0.6	<0.3
74	Nuguini	<0.6	1.7	<0.6	<3	<1	<3	<1.5	<1	<0.6	<0.6	<0.6	3.2
75	Nuguini Fv31.6	<0.6	<1.5	0.6	<3	<1	2.1	<1.5	<1	<0.6	<0.6	<0.6	<0.3
76	Offshore Mou.mix	<0.6	<1.5	<0.6	<3	24.4	13.3	<1.5	1.2	131	<0.6	<0.6	<0.3
77	OffshoreMou..mix50	1.6	<1.5	0.6	<3	22.4	10.1	<1.5	6.3	113	<0.6	0.8	0.6
78	Oseberg	<0.6	<1.5	<0.6	<3	3.8	4.2	<1.5	1	2.7	<0.6	<0.6	<0.3
79	OsebergFv13.9	<0.6	<1.5	1	<3	4.1	4.5	<1.5	<1	2.9	<0.6	<0.6	<0.3
80	Oseberg Fv27.5	<0.6	<1.5	<0.6	<3	5.2	2.6	<1.5	2.8	3.3	<0.6	<0.6	<0.3
81	Panuk crude	<0.6	<1.5	<0.6	<3	<1	<3	<1.5	<1	<0.6	<0.6	<0.6	<0.3
82	Panuk F-99	<0.6	<1.5	<0.6	<3	<1	<3	<1.5	<1	<0.6	<0.6	<0.6	<0.3
83	Pitas point	<0.6	<1.5	3.3	<3	<1	10.3	<1.5	<1	<0.6	<0.6	0.6	0.6
84	Pitas point Fv23.6	<0.6	<1.5	4.1	<3	<1	12.8	<1.5	<1	<0.6	<0.6	1.3	0.75
85	Plate form Irene	<0.6	<1.5	5.1	<3	60.5	44	2.3	237	238	0.8	1.1	53.6
86	Port Hueneme	0.6	<1.5	0.6	<3	68	16	<1.5	3.1	253	<0.6	0.6	<0.3
87	Port Hueneme Fv8.4	1.7	<1.5	0.6	<3	79	19.7	<1.5	20.3	288	<0.6	1.1	0.7
88	Port HuenemeFv14.	0.6	<1.5	0.4	<3	73	15.6	<1.5	3.3	260	<0.6	0.6	<0.3
89	Santa Clara	1.5	<1.5	<0.6	<3	77	115	<1.5	1.8	193	<0.6	<0.6	<0.3
90	Santa ClaraFv11.4	2	<1.5	<0.6	<3	97	155	<1.5	2.6	250	<0.6	2	0.6

91	Santa Clara Fv 21.6	<0.6	<1.5	0.6	<3	101	155	<1.5	3.3	240	<0.6	1.9	0.65
92	Sockeye Crude	2	<1.5	<0.6	<3	42.2	3.6	<1.5	<1	125	<0.6	2	<0.3
93	Sockeye Fv12.5	1.1	<1.5	<0.6	<3	49.3	7.9	<1.5	<1	139	<0.6	3.4	<0.3
94	Sockeye Fv22.0	1.5	<1.5	<0.6	<3	60.7	11.5	<1.5	1	173	<0.6	2	<0.3
95	St.Amble Tire Fireoil	<0.6	1.6	266	<4	<1	25	<1.5	<1	<0.6	<0.6	<0.6	<0.3
96	Sumatran Duri crude	<0.6	<1.5	0.6	<3	30.9	12.9	<1.5	3	1.2	<0.6	<0.6	<0.3
97	Sumatran light Min.	<0.6	<1.5	<0.6	<3	8.5	8	<1.5	2	0.7	2	<0.6	<0.3
98	Synthetic crude	<0.6	<1.5	<0.6	<3	<1	<3	<1.5	1.1	<0.6	<0.6	<0.6	<0.3
99	Taching crude	<0.6	<1.5	<0.6	<3	2.8	11	<1.5	1.6	<0.6	<0.6	<0.6	<0.3
100	Terra Nova	<0.6	<1.5	<0.6	<3	1.3	4.5	<1.5	<1	<0.6	<0.6	0.65	<0.3
101	Transmountain	<0.6	<1.5	<0.6	<3	8.3	5.2	<1.5	2.9	6.2	<0.6	<0.6	0.4
102	Transoil AEC#10	3.6	<1.5	0.6	<3	48.3	13.1	<1.5	14	127	<0.6	1.7	<0.3
103	Udang crude	<0.6	<1.5	2.1	<3	71	<3	<1.5	28	26.8	<0.6	0.9	1.3
104	Waxy light heavy cru	<0.6	<1.5	0.9	<3	56.5	33	<1.5	4.7	46	<0.6	<0.6	0.6
105	Weathered Mou.Mix	<0.6	<1.5	0.8	<3	27.8	13.2	<1.5	2.3	135	<0.6	1.2	<0.3
106	West Texas sour	1.2	<1.5	0.5	<3	4.4	17.8	<1.5	1.1	17.8	<0.6	<0.6	<0.3
107	West Texas sour Fv2	1.3	<1.5	0.7	<3	5.9	28.4	<1.5	2.1	23.8	<0.6	<0.6	<0.3
108	Hugh Brown Diluant	1	<1.5	<0.6	<3	<1	3	<1.5	1.4	<0.6	<0.6	<0.6	<0.3
109	West Texas Interme	<0.6	<1.5	1.1	<3	18.8	22.6	<1.5	24.7	3.2	<0.6	0.76	3.2
110	Gasoline Regular	<0.6	<1.5	0.5	1750	<1	<3	<1.5	<1	<0.6	<0.6	0.54	<0.3

Table 10. Concentrations (ppm) of 9 elements in 30 oil samples

No.	Sample	Se	Cd	Co	Sn	Hg	Mn	Ca	Al	Sr
1	Port Hueneme Crude	<15	<0.5	<1	<15	<15	<0.3	48.8	6.8	0.62
2	Boscan Crude	<15	<0.5	<1	<15	<15	0.52	470	69.9	1.58
3	Platform Irene	<15	<0.5	<1	<15	<15	0.56	291	14	9.96
4	Sockeye Crude	<15	<0.5	<1	<15	<15	<0.3	33.7	<5	0.2
5	Carpenteria crude	39	<0.5	<1	<15	<15	<0.3	170	<5	<0.2
6	Maya crude	<15	<0.5	<1	<15	<15	<0.3	102	9	<0.2
7	Marine Intermediate	<15	<0.5	1.4	<15	<15	<0.3	380	51.7	0.3
8	Nerlerk Fv15.9	<15	<0.5	<1	<15	<15	<0.3	78.3	5.1	0.2
9	Nektoralic Fv9.9%	<15	<0.5	<1	<15	<15	<0.3	72	6.6	<0.2
10	Irane Heavy crude	<15	<0.5	<1	<15	<15	<0.3	82.6	5.4	<0.2
11	Ninian crude	<15	<0.5	<1	<15	<15	<0.3	44.6	<5	<0.2
12	Arabian light Fv24.2	<15	<0.5	<1	<15	<15	<0.3	34.9	<5	<0.2
13	Dos Cudra Fv20.3		<0.5	2.1	<15	<15	<0.3	85.4	<5	<0.2
14	Transmountain blend	<15	<0.5	<1	<15	<15	<0.3	58.7	<5	0.38
15	North slope	24.7	<0.5	<1	<15	<15	<0.3	111	<5	<0.2
16	Hog oil	19.4	<0.5	<1	<15	<15	<0.3	89	130	0.3
17	Bent Horn A02	17	<0.5	<1	<15	<15	0.4	105	<5	0.2
18	West Texas sour	<15	<0.5	<1	<15	<15	<0.3	39.8	<5	<0.2
19	West Texas Intermediate	<15	<0.5	<1	<15	<15	0.4	100	<5	0.38
20	Federated Crude	<15	<0.5	<1	<15	<15	<0.3	54.6	<5	0.25
21	Lago Medio	22	<0.5	<1	<15	<15	<0.3	420	<5	0.2
22	ASMB	18	<0.5	<1	<15	<15	<0.3	53.4	<5	<0.2
23	Oseberg Crude	<15	<0.5	<1	<15	<15	<0.3	58	<5	<0.2
24	California Apl11	23.3	<0.5	<1	<15	<15	0.5	64	5.4	1.13
25	Cold Lake	<15	<0.5	<1	<15	<15	0.5	111	6.3	<0.2
26	BCF24 Fv9.23	21	<0.5	<1	<15	<15	<0.3	48.4	<5	0.37
27	Hondo Fv32.3	<15	<0.5	<1	<15	<15	<0.3	99.5	7.8	0.94
28	Santa clara	<15	<0.5	<1	<15	<15	<0.3	42	<5	0.2
29	Terra Nova	<15	<0.5	<1	<15	<15	<0.3	46	<5	<0.2
30	Taching crude	<15	<0.5	<1	<15	<15	<0.3	54.5	<5	<0.2

oil sample category designation and the microwave digestion conditions for different categories are proposed in Table 7 and 8.

More than 110 oil samples collected from the oilfields of the world have been digested and measured by ICP-AES. Results are listed in Table 9 and 10.

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PROCEDURES FOR MICROWAVE DIGESTION
AND ICP MEASUREMENT OF OIL SAMPLES

The procedures listed below are a brief description of the microwave digestion and ICP measurement of oil samples. The purpose of the instructions is to serve as a quick reference guide for technicians. For more detailed information about ICP-AES instrument, CEM microwave sample preparation system and the methods used to detect trace metals and sulphur in oils by microwave digestion and ICP measurement, the reader may refer to the following documents:

1. User Manual for Model 3410 ICP Spectrometer.

2. CEM Microwave Sample Preparation System.

3. Microwave digestion and ICP measurement of oil samples ---- The first part of this report.

Microwave Digestion of Oils

Microwave digestion of oil samples is performed using the CEM Microwave Sample Preparation System (Model MDS-2000), including CEM lined digestion vessels.

Before microwave digestion:

1) Remove the vent stem from the vessel cover and install a single rupture

membrane. It is important to use a new rupture membrane for each sample run.

2) Once the rupture membrane is in place, thread the vent stem back into the cover until hand tight.

3) Weigh the oil sample 0.2 g (with accuracy of 0.001 g) and place it into the vessel liner.

4) Add 10 ml of nitric acid (70%) into the vessel liner.

5) Place the vessel cover (with rupture membrane and vent stem installed) on top of the vessel liner.

6) Thread the vessel cap onto the vessel body until hand tight.

7) Insert the vent tube into the small exit port located on the side of the vessel cover.

8) Place the complete vessel assembly into the turntable, orienting the vent tube towards into the centre of the turntable.

9) Repeat steps 1-8 for the remaining vessels.

10) Place the turntable, with a maximum of 6 vessels, into the microwave system cavity.

11) Choose one vessel, which is expected to show a pressure rise more quickly than others (based on the dependence of the Time-Pressure curves on the density, viscosity and the amount of oil samples) for pressure monitoring.

Microwave Digestion Conditions:

1) Heating rate at 70% of total microwave power.

2) Keep the pressure inside of the vessel at 190 psi for 30 minutes.

After Microwave Digestion:

1) After completion of the digestion, allow the vessels to remain in the microwave system for about 45-60 minutes with the microwave power off.

2) Turn the microwave system exhaust fan to the maximum speed setting and ensure the turntable is not rotating.

3) Manually vent the pressure monitoring vessel by turning the vent stem slowly counter-clockwise to a partially open position and close the microwave oven door as soon as possible.

4) When the pressure reading on the screen of the microwave oven is reduced to zero, open the door and transfer all of the vessels into the fume hood.

5) Manually vent remaining vessels in the fume hood.

6) Dilute the digested solution to total volume of 50.0 ml with deionized water and store it for ICP measurement.

ICP Measurement for Digested Oil Samples

ICP-AES measurement for detection of trace metals and sulphur in the digested oil samples is performed using ARL 3410 ICP Spectrometer.

ICP Instrument Configuration Setup:

1) General Parameters:

Vacuum/Air Path   Air (Nitrogen purged)

Grating Coefficient   1.000012

Grating Ruling	2400
Steps/Revolution	0.999883
Number of teeth on gear	390
Number of steps on gear	25000
Number of Filters	5
Default measure step size	0.0028125 nm

2) Zero Order Parameters:

Zero search Start Step	76151
Search Step Increment	5
Integration time	0.3 sec.
PMT setting	0

3) Reference Line Parameters:

Reference line wavelength	355.431 nm
Search Range	0.080 nm
Integration time	0.5 sec.
PMT Setting	10
Filter Setting	2

ICP Operation Parameters

    1) RF Power

Reflected Power	0 to 10 W
Forward Power	650 W
Plate Volts	3000-3900 V
Plate Current	350 to 450 mA
Grid Current	65-120 mA
Drive Volts	3.5 to 4.0 V

2) Argon Gas Flows

Coolant	7.5 L/min.
Plasma	0.8 L/min.
Carrier	0.8 L/min.

3) Sample uptake rate   2.0-2.5 ml/min.

Procedures for Unknown Sample Measurement

Steps for Turning on the Plasma:

1) Turn on the computer. The ARL logo and a picture of a plasma torch should be displayed on the screen.

2) Check the main power of ICP-AES 3410 instrument. The main power should be connected to a 220 V single phase, 50 amp, AC line.

3) Check the purge gas (Nitrogen) pressure, which should be higher than 60 psi.

4) Check the torch alignment with respect to the induction coil.

5) Check the four safety interlocks (Water, Argon, TCU and Door) on the front panel. All four indicator lights should be on. Make sure that the water is flowing through the induction coil; the argon pressure of the main flow is higher than 65 psi; the Tuning Coupling Unit (TCU) is working properly and the torch box door is closed.

6) Check the sample introduction system, including uptake tube, nebulizer, spray chamber and drain system.

7) Ensure the uptake tube is submerged in deionized water. Press the START button on the front panel to ignite the torch.

8) Check the pressure gauge readings of the coolant gas (30 psi), plasma (24 psi) and carrier (45 psi).

9) Record the value for the Incident Watts, Reflected Watts, Plate Volts, Plate Current, Grid Current, and Drive Volts as ICP Daily parameters.

Steps for the Analysis of Unknown Samples:

1) Spectrometer Profile

From the main menu choose the ANALYZE section, then press <F4> to profile the spectrometer. When profiling is finished, an average location of the argon line at 335.431 nm will be shown along with a zero position. Save the profiling results and record it as daily ICP parameters.

2) From the ANALYZE section choose the MANUAL option, then press <F1>. The screen will display the names of all the tasks which have been defined. There are 6 defined tasks available. Each task measures a specific combination of metals. The tasks

were created by setting measurement parameters, selection of emission lines and calibration with standard solutions. The followings are lists of the tasks and their corresponding selected wavelengths.

Task name   OILCAO02

Mg   279.553 nm

V   309.311 nm

Cr   267.716 nm

Mn   257.610 nm

Fe   259.940 nm

Co   228.616 nm

Ni   231.604 nm

Zn   213.856 nm

Cd   214.438 nm

Hg   253.652 nm

Pb   220.353 nm

Task Name   OILCAO03

Al   396.152 nm

P   213.618 nm

Ti   337.280 nm

V   309.311 nm

Cr   267.716 nm

Ni   231.604 nm

Cu   324.754 nm

As   193.759 nm

Mo   202.030 nm

Sn   242.949 nm

Ba   455.403 nm

Task Name OILCAO04

Mg   279.553 nm

P   213.618 nm

Ti   337.280 nm

V   309.311 nm

Cr   267.716 nm

Fe   259.940 nm

Ni   231.604 nm

Cu   324.754 nm

Zn   213.856 nm

Mo   202.030 nm

Ba   455.403 nm

Pb   220.353 nm

Task Name OILCAO05

Al   396.152 nm

Ca   393.366 nm

Mn   257.610 nm

Co   228.616 nm

Se   196.090 nm

Sr   407.771 nm

Nb   295.088 nm

Cd   214.438 nm

Sn   242.949 nm

Hg   253.652 nm

Task Name OILSULFR

S   182.037 nm

Task Name VGCAO

Cu   324.754 nm

Zn   213.856 nm

Cd   214.438 nm

Sn   242.949 nm

Pb   220.353 nm

3) After setting the default task, press <F2> to start the unknown sample measurement sequence.

4) Press <F2> again for the drift correction of the calibration curves.

5) According to the requirement in the drift correction procedure, run low reference and high reference solutions.

6) After completion of the drift correction procedures, the drift correction factors will be displayed. Press <F1> for the blank and unknown samples measurement. The results will be printed out and saved on the hard disc automatically during the sample measurement.

7) When the sample measurement finished, transfer the uptake tube from the sample into the nitric acid solution (1N). Allow the nitric acid to clean the sample introduction system for at least 10 minutes. Then transfer the uptake tube to the deionized water container. The instrument is now ready for another task measurement. (Note: If the uptake tube is removed from solution for an extended time period, the plasma torch will automatically turn off.)

APPLICATION OF ICP-AES TO ANALYSIS OF COMPOUNDS
IN THE CHEMICAL SPILL PRIORITY LIST

Aluminium Chloride $AlCl_3$

Its diluted water solution can be detected by ICP-AES using Al emission lines at 309.28, 396.15, 237.32, 226.92 308.22 and 394.40 nm.

Aluminium chloride in soil can be dissolved in water, then measured by ICP-AES.

Aluminium Sulfate

$Al_2(SO_4)_3$ is soluble in water and can be detected by ICP-AES from both of Al line 308.21 nm and S line 182.04 nm.

Aluminium sulfate in soil can be dissolved by dilute HNO_3 then measured by ICP-AES.

Arsenic Acid

Arsenic acid is freely soluble in water. Arsenic acid in dilute HNO_3 solution can be detected by ICP-AES using typical As line at 193.76 nm with detection limit less than 1 ppm.

Arsenic acid in soil can be extracted by dilute HNO_3 acid then measured by ICP-AES.

Asbestos

Asbestos has complicated compositions: $[Mg_6(Si_4O_{10})(OH)_8]$, $[(Mg,Fe)_7(Si_8O_{22})(OH)_2]$, $[Ca(Mg,Fe)_5(Si_8O_{22})(OH)_2]$. Asbestos is not water soluble. Trace of Mg, Ca, Fe, Na may be detectable in water, which contains asbestos, by ICP-AES, but it is usually difficult to identify whether those metal elements originated from asbestos. Asbestos in soil could be determined by ICP-AES after digestion of the samples based on fusion of the sample or on the dissolution of the sample using hydrofluoric acid or by the recently developed microwave digestion method. Following spectral lines are recommended for measuring the major elements: Si 288.16 nm, Al 308.22 nm, Fe 259.94 nm, Ca 317.93 nm, Mg 279.09 nm, Na 588.99 nm.

Azinphos ethyl and Azinphos methyl
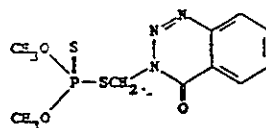
The solubility of azinphos methyl is very small (33 mg/L at 25°C), the maximum concentration of P and S in water would be around 3 ppm and 6 ppm respectively, and should be detectable by ICP-AES using UV lines of P at 179.29 nm and line of S at 182.04 nm. The measurement of Azinphos methyl can be improved by extraction using organic solvent. Azinphos methyl in soil can be dissolved in organic solvent then digested for ICP-AES measurement.

Barium Sulfate $BaSO_4$

The solubility of $BaSO_4$ in water is about 2.5 ppm. It is theoretically possible to detect $BaSO_4$ in water by ICP-AES using the most sensitive line 455.4 nm with detection limit below 1 ppm. Barium sulfate in soil can be dissolved by dilute HNO_3 acid then determined by ICP-AES.

Borax $B_4Na_2O_7$

Borax in water is quite soluble (1 g/16 mL). Borax in water should be measurable by ICP-AES using B lines (249.77 nm and 249.67 nm) and Na line 588.99 nm. Borax in soil can be extracted by water then measured by ICP-AES. The fused borax or borax glass sample can be treated using anhydrous potassium carbonate and perchloric acid then diluted for ICP-AES measurement.

Cadmium Cd

Trace cadmium can be detected from water by ICP-AES using Cd lines at 214.44, 228.80 and 226.50 nm. The Cd 226.5 nm line is normally used, the Cd 228.8 nm line may have interferences from As.

Cadmium Sulfate $CdSO_4$

Cadmium sulfate is freely soluble in water. $CdSO_4$ in water should be easily determined by ICP-AES using Cd line at 214.44, 228.80, 226.50 nm. S in SO_4 also can be detected using S line at 182.04 nm. $CdSO_4$ in soil can be dissolved in water then measured by ICP-AES.

Calcium Arsenate $Ca_3(AsO_4)_2$

Calcium arsenate is slightly dissolved in water (0.013 g/100 c.c.). This concentration should be measurable by ICP-AES using Ca lines at 393.37, 396.85, 317.93, 422.67 and 315.89 nm and As line at 193.76 nm. Calcium arsenate in soil can be dissolved in dilute HNO_3 solution then measured by ICP-AES.

Calcium carbide CaC_2

CaC_2 is not stable in water and reacts with water generating C_2H_2. Therefore, calcium carbide is not measurable in water. Calcium carbide in soil can be dissolved by diluted acid then detected by ICP-AES using Ca lines. However, Calcium carbide is easily determined through C_2H_2 generated by its reaction with water.

Calcium Chloride $CaCl_2$

Calcium chloride in water can be determined by ICP-AES using Ca lines: 393.37, 396.85, 317.93, 422.67 and 315.89 nm. Calcium chloride in soil can be dissolved by water then measured by ICP-AES.

Calcium Cyanide $Ca(CN)_2$

Calcium cyanide is soluble in water with gradual liberation of very poisonous HCN. Calcium cyanide in water can theoretically be measured by ICP-AES using Ca lines, but it is not recommended due to the poisonous HCN liberated.

Calcium hydroxide $Ca(OH)_2$

Although the solubility of $Ca(OH)_2$ in water is limited (0.185 g/100 c.c.H_2O at 25^0C), the calcium is easily measured by ICP-AES using Ca lines. Calcium hydroxide in soil can be dissolved by dilute acid (HNO_3 or HCl) then measured by ICP-AES.

Calcium hypochlorite $CaCl_2O_2$, Calcium nitrate $Ca(NO_3)_2$, Calcium oxide CaO

These calcium compounds in water or in soil can be detected by ICP-AES using the methods similar to that of $CaCl_2$ and $Ca(OH)_2$ measurements described above.

**Calcium phosphate $CaHPO_4$, $Ca(H_2PO_4)_2$, $Ca_3(PO_4)_2$**

Calcium phosphate in water can be detected by ICP-AES using Ca lines and P line

(182.04 nm). Calcium phosphate in soil can be treated by dilute HCl or HNO$_3$ then measured by ICP-AES.

Cesium^{137} Cs^{137}

Cs^{137} is radiative, T$_{1/2}$=30 years. Cesium ion in water , in principle, can be detected by ICP-AES using Cs lines. However, it is not recommended to detect Cs^{137} by ICP, because Cs^{137} can be easily detected through its radiation measurement.

Chlorpyrifos
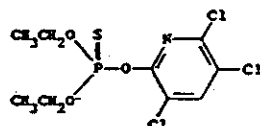
The maximum concentration of chlorpyrifos in water at 25^{0}C is about 2 ppm. The maximum concentration of P and S can be estimated to be around 90 ppb. Therefore, it would be difficult to directly detect chlorpyrifos in water by ICP-AES through their P lines(179.29, 178.30 nm) and S lines(182.04, 180.70 nm). Preconcentration through extraction of organic solvent and further digestion to prepare a suitable sample containing detectable amount of P and S by ICP-AES may be possible for detecting trace of chlorpyrifos in water. Chlorpyrifos in soil could be extracted by organic solvent and concentrated, then digested to prepare suitable liquid sample for ICP-AES measurement.

Chromic acid

Chromic acid is very soluble in water and should be easily determined by ICP-AES using Cr lines: 205.55, 206.15, 267.72 nm, with good sensitivity. Cr 267.7 nm line has been widely used. Chromic acid in soil , in principle, can be detected by ICP-AES after transferring it into water or dilute acid solution.

Cobaltous nitrate Co(NO$_3$)$_2$

Cobaltous nitrate is soluble in water, therefore, it can be easily detected from water by ICP-AES using Co lines 238.89, 228.62 nm. The Co line 228.62 has been most commonly used with less spectral interference. Cobaltous nitrate in soil can be transferred into water or dilute acid solution then measured by ICP-AES.

Copper chloride CuCl$_2$ (cupric chloride), CuCl (cuprous chloride)

CuCl$_2$ is soluble in water, CuCl is sparingly soluble in water. Both CuCl$_2$ and CuCl in water are measurable by ICP-AES using Cu lines at 324.75, 224.70 nm. The Cu atom line 324.75 nm is most sensitive with wide dynamic range and is essentially free from spectral

interferences. $CuCl_2$ and $CuCl$ in soil can be dissolved in dilute acid (HNO_3 or HCl) solutions, then measured by ICP-AES.

Copper cyanide CuCN

Because CuCN is not water soluble, it is difficult to be measured from water. CuCN in soil could be treated with HNO_3 to convert it to $Cu(NO_3)_2$ solution, but care must be taken during the sample digestion, because of the poisonous HCN liberated. Cu^{2+} solution can be measured by ICP-AES using Cu lines.

Cupper sulfate CuSO₄

$CuSO_4$ is soluble in water forming a blue color solution. Trace of $CuSO_4$ in water can be detected by ICP-AES using Cu lines (224.70, 324.75 nm) and S line (182.04 nm). $CuSO_4$ in soil can be extracted by water then measured by ICP-AES.

Coumaphos
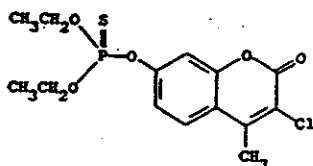
Coumaphos is practically insoluble in water and difficult to be directly detected from water. It may be detectable by ICP-AES using S lines(180.70, 182.04 nm) and P lines (178.30, 179.29, 213.62, 214.91 nm) after preconcentration through the extraction by organic solvent. Coumaphos in soil could be extracted by organic solvent and concentrated then digested to prepare a suitable liquid sample for ICP-AES measurement.

Demeton
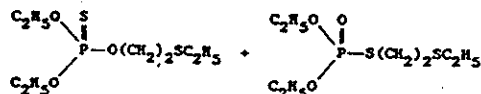
Demeton is virtually insoluble in water. It would be very difficult to be directly detected, but it may be detectable by ICP-AES using P lines: 178.30, 179.29, 213.62, 214.91 nm) and S lines (180.70, 182.04 nm) after preconcentration through organic solvent extraction. Demeton in soil can be dissolved in organic solvent then digested and measured
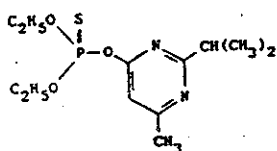
by ICP-AES.

Diallate

$(CH_3)_2CH$
$NCOSCH_2CCl=CHCl$
$(CH_3)_2CH$
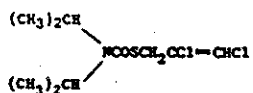
Diallate is slightly soluble in water(40 ppm). It may be detectable by ICP-AES using S lines (180.70,182.04 nm). Diallate in soil can be dissolved in organic solvent then digested for ICP-AES measurement.

Diazinon

C_2H_5O S
$P-O$ $CH(CH_3)_2$
C_2H_5O
CH_3

The solubility of diazinon in water at 25^0C is about 0.004% (40 ppm). The content of S and P is around 4 ppm and may be detectable by ICP-AES using P lines(178.30, 179.29, 213.62, 214.91 nm) and S lines (180.70, 182.04 nm). Diazinon in soil can be dissolved in organic solvent (ethers), then digested for ICP-AES measurement.

Dichlorvos

CH_3O O
$P-O-CH=CCl_2$
CH_3O
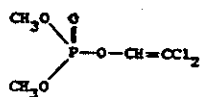
Dichlorvos is soluble in water (1 g/100 c.c.) and should be measurable in water by ICP-AES using P lines and S lines. Dichlorvos in soil can be dissolved in organic solvent then digested for ICP-AES measurement.

Dicrotophos

CH_3O O
$P-O$
CH_3O
$C=C$ H
H_3C $CON(CH_3)_2$
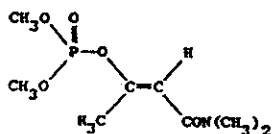
Dicrotophos is water soluble and can be detected from water by ICP-AES using P lines (178.30, 179.29 nm). Dicrotophos in soil can be dissolved in water or in organic solvent then digested at below 90^0C for ICP-AES measuerment.
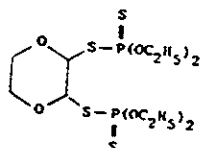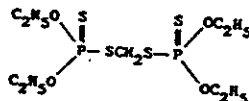
Dioxathion

Dioxathion is practically insoluble in water. It would be difficult to be directly detected from water by ICP-AES through P lines and S lines. Dioxathion in soil can be extracted by organic solvent (hexane), then digested for ICP-AES measurement.

Disulfoton
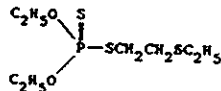
Disulfoton is insoluble in water and it may not be measurable from water by ICP-AES using S lines and P lines. Disulfoton in soil may be extracted by organic solvent then digested for ICP-AES measurement.
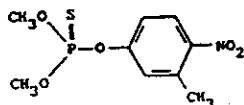
Ethion

Ethion is slightly soluble in water. Ethion in water should be measurable by ICP-AES through P lines and S lines. Ethion in soil can be extracted by organic solvent (xylene, acetone, etc.) and digested for ICP-AES measurement.

Ethyl mercaptan CH₃CH₂SH

The solubility of ethyl mercaptan in water is 6.76 g/ L at 20°C. Ethyl mercaptan in water is measurable by ICP-AES using S lines (180.70, 182.04nm). Ethyl mercaptan in soil can be dissolved by ethanol or ethers then digested for ICP-AES measurement.

Fenitrothion

Fenitrothion is practically insoluble in water, it would be difficult to be directly detected from water by ICP-AES through S lines and P lines. Fenitrothion in soil could be extracted by most organic solvents then digested for ICP-AES measurement.

Ferric chloride FeCl₃

Ferric chloride is readily soluble in water. $FeCl_3$ in water can be easily determined by ICP-AES through Fe lines: 238.20, 239.56, 259.94, 234.35, 240.49, 259.84 and 261.19 nm. The most widely used Fe line is probably the 259.94 nm. The most sensitive Fe line is at 238.30 nm. Ferric Chloride in soil can be dissolved in dilute acid (HNO_3 or HCl) then measured by ICP-AES.

Ferric oxide Fe₂O₃

Ferric oxide in water or in soil can be determined by ICP-AES. The procedure for measurement is similar to that for ferric chloride.

Ferric sulfate FeSO₄

$FeSO_4$ is water soluble. $FeSO_4$ in water can be measured by ICP-AES using Fe lines and S lines. $FeSO_4$ in soil can be dissolved in water or in dilute acid solution then measured by ICP-AES.

Fonofos
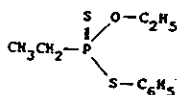
Fonofos is practically insoluble in water. Fonofos in water may not be detected directly by ICP-AES through P lines and S lines. Fonofos in soil can be dissolved or extracted by organic solvents then digested for ICP-AES measurement.

Hydrogen sulfide H_2S

H_2S is dissolvable in water (one gram H_2S in 187 c.c. water at 10^0C), and can be detected by ICP-AES using S lines. Trace of H_2S could be absorbed by soil and can be detected after dissolved in water, then measured by ICP-AES. However, the detection of H_2S by ICP-AES is not recommended because there are more easy and efficient methods available.

Lead oxide PbO_2, PbO

Neither PbO_2 nor PbO are water soluble, therefore, they may not be measurable from water. PbO_2 or PbO in soil can be treated by dilute HNO_3 then measured by ICP-AES using lead line at 220.35 nm.

Magnesium hydroxide $Mg(OH)_2$

$Mg(OH)_2$ is practically insoluble in water (0.0009 g/100c.c.). The maximum concentration of Mg in water is 3.7 ppm. In the case where there are no large interferences from another elements, $Mg(OH)_2$ in water should be detectable through the Mg lines: 279.55, 280.27, 285.21, 279.81, 202.58, 279.09, 383.83 nm. $Mg(OH)_2$ in soil can be dissolved by dilute acid then measured by ICP-AES.

Malathion
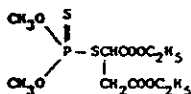
Malathion is slightly soluble in water(145 ppm), and could be measurable from water by ICP-AES through P lines (178.30, 179.29, 213.62,214.91 nm) and S lines180.70, 182.04 nm). Malathion in soil can be extracted by organic solvent then digested for ICP-AES measurement.

Maneb
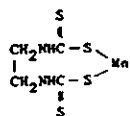
Maneb is moderately soluble in water and can be measured from water by ICP-AES using both of Mn lines (257.61, 259.37, 260.57nm) and S lines (180.70,182.04nm). Maneb in soil can be extracted by chloroform or pyridine then digested for ICP-AES measurement.

Mercuric acetate $Hg(CH_3COO)_2$

Mercuric acetate is soluble in water (one gram dissolves in 2.5 ml cold water), and can be measured by ICP-AES using Hg lines: 194.2, 184.96 nm. Mercuric acetate in soil can be dissolved by hot water then measured by ICP-AES.

Mercuric chloride $HgCl_2$

$HgCl_2$ is water soluble (one gram dissolves in 13.5 ml water). $HgCl_2$ in water can be measured by ICP-AES using Hg lines (194.20,184.96 nm). $HgCl_2$ in soil can be dissolved by dilute HCl solution then measured by ICP-AES.

Mercuric thiocyanate $Hg(SCN)_2$

$Hg(SCN)_2$ is slightly soluble in cold water (0.069 g/100 c.c.) and is measurable by ICP-AES using Hg lines (194.2, 184.96 nm) or S lines (180.70,182.04 nm). $Hg(SCN)_2$ in soil can be well dissolved in dilute HCl solution then measured by ICP-AES.

Mercurous nitrate $Hg_2(NO_3)_2$

Mercurous nitrate is soluble in water forming a basic salt and can be detected by ICP-AES using Hg lines (194.2,184.96 nm). Mercurous nitrate in soil can be dissolved by dilute acid (dilute HNO_3) then measured by ICP-AES.

Mercury Hg

Mercury is not soluble in water. Trace of mercury could be suspended or adsorbed

by some solid in water and could be detected by ICP-AES using Hg lines after treatment with HNO_3 acid. The mercury in soil can be dissolved by HNO_3 acid then measured by ICP-AES.

Methyl parathion
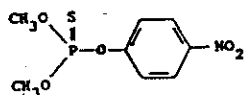
Methyl parathion is slightly soluble in water (50 ppm). It may be detected in water by ICP-AES using P lines (178.29, 213.62 and 214.91 nm) and S lines (180.70, 182.04 nm). Methyl parathion in soil can be extracted by organic solvent then digested for ICP-AES measurement.

Mevinphos
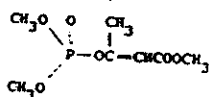
Mevinphos is soluble in water, it should be measurable in water by ICP-AES using P lines (178.29, 213.62, 214.91 nm). Mevinphos in soil can be extracted by organic solvent then digested for ICP-AES measurement.

Naled
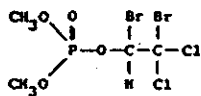
Naled is practically insoluble in water, but completely hydrolysed by water within 48 hrs. Naled in water may be identified through its hydrolysed product, which should be detectable by ICP-AES through P lines (178.29, 213.62, 214.91 nm). Naled in soil can be extracted by aromatic hydrocarbon solvent then digested for ICP-AES measurement.

Nickel carbonyl Ni(CO)$_4$

Nickel carbonyl is slightly soluble in water (1/5000) free from air. It would be

oxidized in the air. Nickel carbonyl may be measurable by ICP-AES using Ni lines: 221.65, 232.00, 231.60 nm. The 231.60 nm is the most popular line for ICP-AES , essentially no significant interference expected. Nickel carbonyl in soil can be dissolved in several organic solvents (alcohol, acetone, CCl_4 etc) then digested for ICP-AES measurement.

Parathion, ethyl
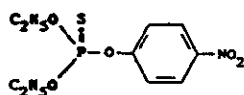
Parathion is practically insoluble in water (20 ppm). The maximum concentration of S and P is around 2 ppm. Parathion in water may be detectable by ICP-AES using S lines and P lines. Parathion in soil could be extracted by organic solvents (alcohols, ethers, aromatic hydrocarbons) then digested for ICP-AES measurement.


p-Phenolsulfonic acid
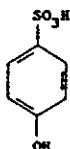
Phenolsulfonic acid in water can be measured by ICP-AES using S lines. Phenolsulfonic acid in soil can be dissolved by water then digested for ICP-AES measurement.

Phenyl mercuric acetate $C_6H_5HgOOCCH_3$
Phenyl mercuric acetate in water can be determined by ICP-AES using Hg lines (194.2 nm, 184.96 nm). Phenyl mercuric acetate in soil can be extracted by organic solvents (alcohol, benzene, acetone) then digested for ICP-AES measurement.

Phosphamidon
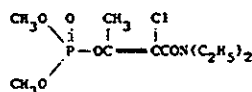
Traces of phosphamidon in water can be directly detected by ICP-AES using P lines

(178.29, 213.62, 214.91nm). Phosphamidon in soil can be dissolved in water then digested for ICP-AES measurement.

Phosphoric acid H_3PO_4

Trace H_3PO_4 in water can be detected by ICP-AES using P lines (178.29, 213.62, 214.91 nm). Phosphoric acid in soil can be dissolved in water then measured by ICP-AES.

Phosphorus P

The solubility of P in water is about 3 ppm, it would be difficult to be directly detected from water by ICP-AES using P lines. The signal observed from P lines may not be originated from phosphorus but most probably from PO_4^{-3}, HPO_4^{-2}, or $H_2PO_4^{-1}$. Phosphorus in soil can be oxidized and dissolved by HNO_3 then measured by ICP-AES.

Phosphorus pentoxide P_2O_5

Phosphorus pentoxide can not exist in water, immediately exothermic hydrolysis by water to form phosphoric acid. The suspicious spill of phosphorus pentoxide into water may be identified through the determination of phosphoric acid in water by ICP-AES using P lines (178.29,213.62,214.91 nm). Phosphorus pentoxide in soil can be dissolved and extracted by dilute acid then measured by ICP-AES.

Potassium carbonate K_2CO_3

Potassium carbonate is soluble in water, therefore, it can be measured from water by ICP-AES using K line (766.49 nm). Potassium atoms, in ICP source, are easily ionized, so that only a small proportion of potassium is in the atomic state, hence sensitivity for K is low. For trace levels of potassium (below 500 ppb) it would be difficult to detect. Potassium carbonate in soil can be extracted by cold water then measured by ICP-AES.

Potassium chloride KCl

KCl is water soluble, it can be measured from water by ICP-AES using K line at 766.49 nm with less interferences from Na, Mg, and Ca. Since the sensitivity of this atomic K line is low, trace KCl (below 500 ppb) would be difficult to measure. Potassium in soil

can be dissolved in water then measured by ICP-AES.

Potassium cyanide KCN

The suspicious spill of the violent poisonous KCN in water can be detected by ICP-AES using K line at 766.49 nm. In order to identify KCN, it is better to detect CN^{-1} using another method. Potassium cyanide in soil can be extracted by water then measured by ICP-AES.

Potassium hydroxide KOH

The potassium hydroxide in water can be measured by ICP-AES using K line 766.49 nm after neutralization with dilute HNO_3 acid. Potassium hydroxide in soil can be dissolved by water or dilute HNO_3 acid solution then measured by ICP-AES.

Potassium permangate $KMnO_4$

$KMnO_4$ in water can be measured by ICP-AES using K line (766.49 nm) and Mn lines (257.61, 259.37, 260.57 nm). For Mn the most sensitive line is 257.61 nm. This has been popularly used. The detection limit for Mn (10-100 ppb) is much lower than that of K, therefore, measurement with Mn line is essential. $KMnO_4$ in soil can be dissolved in water or in dilute acid solution then measured by ICP-AES.

Sodium aluminate $NaAlO_2$

Sodium aluminate in water can be measured by ICP-AES using Na lines and Al lines. Na lines at 588.99 and 589.59 nm can be used with less interferences from K, Mg, and Ca. Al lines at 309.28, 396.15, 237.32 226.92, 308.22 and 394.40 nm can be selected. Sodium aluminate in soil can be dissolved by water then neutralized and acidified to prepare suitable solution for ICP-AES measurement.

Sodium arsenite $NaAsO_2$

Sodium arsenite is very poisonous and freely soluble in water. Trace $NaAsO_2$ in

water can be measured by ICP-AES using Na lines(588.99, 589.59 nm) and As lines (193.76, 197.20, 228.82 nm). $NaAsO_2$ in soil can be dissolved in water then measured by ICP-AES.

Sodium azide NaN_3

Sodium azide is soluble in water (40.16% at 10^0C). It should be detectable from water by ICP-AES using Na lines at 588.99, and 589.59 nm. NaN_3 in soil can be extracted by water then measured by ICP-AES.

Sodium borohydride $NaBH_4$

$NaBH_4$ is quite soluble in water (55% at 25^0C). $NaBH_4$ in water can be determined by ICP-AES using Na lines (588.99, 589.59 nm) and B lines (249.77, 249.67 nm). The detection limit of B lines is much lower than that of Na, therefore, using B lines to measure $NaBH_4$ is essential. Sodium borohydride in soil can be extracted by water then measured by ICP-AES.

Sodium carbonate Na_2CO_3, Sodium Hydroxide NaOH, Sodium nitrate $NaNO_3$, Sodium chloride NaCl, Sodium chlorate $NaClO_3$, Sodium hypochloride NaClO

These sodium compounds in water can be measured by ICP-AES using Na lines (588.99, 589.59 nm), except that Na_2CO_3 and NaOH solution should be acidified before ICP-AES measurement. These sodium compounds in soil can be dissolved in water then measured by ICP-AES.

Sodium chromate Na_2CrO_4

Sodium chromate in water can be measured by ICP-AES using Na lines (588.99, 589.59 nm) and Cr lines(205.55, 206.15, 267.72 nm) after the water solution acidified. The sensitivity of Cr line 267.72 nm is much higher than that Na lines. Therefore, measurement of $NaCrO_4$ from Cr lines is essential. Sodium chromate in soil can be extracted by water or dilute acid solution then determined by ICP-AES.

Sodium cyanide NaCN

NaCN is freely soluble in water. NaCN in water is theoretically measurable by ICP-AES using Na lines at 588.99 and 589.59 nm. Because of toxicity of NaCN, it is not recommended to measure NaCN by ICP-AES except for trace level of NaCN. NaCN in soil can be dissolved by water then diluted for ICP-AES measurement.

Sodium dichromate $Na_2Cr_2O_7$

Sodium dichromate in water can be determined by ICP-AES using Na lines (588.99 and 589.59 nm) and Cr lines (205.55, 206.15, 267.72 nm) after acidified with dilute acid (HCl or HNO_3). The sensitivity of Cr lines is much higher than that of Na lines, measurement using Cr lines is essential. $Na_2Cr_2O_7$ in soil can be extracted by water or dilute acid then measured by ICP-AES.

Sodium fluoride NaF

NaF in water is measurable by ICP-AES using Na lines (588.99, 589.59 nm). NaF in soil can be dissolved in water then measured by ICP-AES.

Sodium hydrosulfite $NaHSO_2$

Sodium hydrosulfite in water can be measured by ICP-AES using Na lines (588.99 and 589.59 nm) and S lines (180.70, 182.04 nm). Sodium hydrosulfite in soil can be extracted by water then measured by ICP-AES.

Sodium phosphate Na_3PO_4, Na_2HPO_4, NaH_2PO_4

Sodium phosphate in water can be determined by ICP-AES using Na lines (588.99, 589.59 nm) and P lines (178.29, 213.62 and 214.91 nm). Sodium phosphate in soil can be dissolved by water or dilute acid then measured by ICP-AES.

Sodium silicate Na_2SiO_3, $Na_6Si_2O_7$, $Na_2Si_3O_7$

Sodium silicate in water can be measured by ICP-AES using Na lines (588.99, 589.59 nm) and Si lines (251.61, 288.16, 250.69, 252.85 nm). The 251.61 nm line appears to be the most sensitive Si line, but the 288.16 nm line is most popularly used. Sodium silicate in soil is difficult to be quantitatively measured because the interferences from soil which contains significant amount of Na and Si.

Sodium sulfite Na_2SO_3

Sodium sulfite in water can be measured by ICP-AES using Na lines (588.99 and 589.59 nm) and S lines (180.70, 182.04 nm). Sodium Sulfite in soil can be extracted by water then measured by ICP-AES.

Sulfur S

Sulfur is insoluble in water, but trace of sulfur could exist in water in the form of colloid and may be measurable by ICP-AES using S lines (180.70, 182.04 nm) after digestion by HNO_3/HCl solution. Sulfur in soil can be extracted by some solvents (benzene, acetone) then digested for ICP-AES measurement.

Sulfur dioxide SO_2

SO_2 can be dissolved in water and could be detected by ICP-AES using S lines (180.70, 182.04 nm)
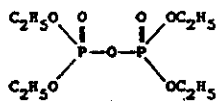
Sulfuric acid H_2SO_4

Sulfuric acid in water can be measured by ICP-AES using S lines (180.70, 182.04 nm) Sulfuric acid in soil can be extracted by water then measured by ICP-AES.

Tetraethyl lead $Pb(C_2H_5)_4$

Tetraethyl lead is practically insoluble in water. Traces of tetraethyl lead in water may be detectable by ICP-AES using Pb line at 220.35 nm after preconcentration of the

sample through extraction with organic solvent. Tetraethyl lead in soil can be extracted by organic solvent (benzene, gasoline) then digested for ICP-AES measurement.

Tetraethyl pyrophosphate

Tetraethyl pyrophosphate can be easily dissolved in water and hydrolysed quickly. Tetraethyl pyrophosphate in water or its hydrolysed product can , in principle, be detected by ICP-AES using P lines (178.29, 213.62, 214.91 nm). Tetraethyl pyrophosphate in soil can be extracted by most organic solvents then digested for ICP-AES measurement.

Thallium sulfate Tl_2SO_4

Thallium sulfate in water can be determined by ICP-AES using Tl lines (351.92, 276.79 nm) and S lines (180.70, 182.04 nm) Thallium sulfate in soil can be dissolved in hot water then measured by ICP-AES.

Thioglycolic acid $HSCH_2COOH$

Thioglycolic acid in water can be determined by ICP-AES using S lines(180.70, 182.04 nm). Thioglycolic acid in soil can be dissolved by water then measured by ICP-AES.

Thiram
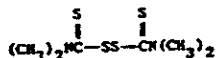
Thiram is insoluble in water. It may not be directly measurable from water by ICP-AES using S lines (180.70, 182.04 nm) unless the sample was preconcentrated by organic solvent extraction. Thiram in soil can be extracted by organic solvent (chloroform, acetone) then digested for ICP-AES measurement.

Titanium dioxide TiO_2

TiO_2 is insoluble in water. TiO_2 in water may not be directly detected by ICP-AES. TiO_2 in soil can be dissolved in hot concentrated H_2SO_4 then diluted for ICP-AES measurement.

Tributyl phosphate $(C_4H_9)_3PO_4$

Tributyl phosphate in water can be determined by ICP-AES using P lines (178.29, 213.62, 214.91 nm). Tributyl phosphate in soil can be dissolved by organic solvents then digested for ICP-AES measurement.

Trichlorfon
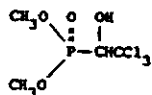
The solubility of trichlorfon in water is 15.5 g/100 ml at 25^0C. Trichlorfon in water can be measured by ICP-AES using P lines (178.29, 213.62, 214.91 nm). Trichlorfon in soil can be dissolved in water then measured by ICP-AES.

Uranyl nitrate $UO_2(NO_3)_2$

Uranyl nitrate in water can be detected by ICP-AES using U lines at 385.96, 367.01, and 263.55 nm. Uranyl nitrate in soil can be extracted by alcohol or ether then digested for ICP-AES measurement.

Vanadium pentoxide V_2O_5

Vanadium pentoxide is water soluble (one gram in about 125 ml water). Vanadium pentoxide in water can be determined by ICP-AES using V lines at 309.31, 310.23, 292.40 and 290.88 nm. V_2O_5 in soil can be dissolved by water or acid then measured by ICP-AES.

Zinc cyanide Zn(CN)$_2$

$Zn(CN)_2$ is almost insoluble in water (0.0005 g/100 ml). It may be detected by ICP-AES using Zn lines (213.86, 202.55, 206.20 nm). Zinc cyanide in soil can be dissolved by alkali hydroxides and may be detectable by ICP-AES using Zn lines.

Zinc chloride ZnCl$_2$

Zinc chloride in water can be determined by ICP-AES using Zn lines (213.86, 202.55, 206.20 nm). The most sensitive Zn line is at 213.86 nm, but there is small interference from Cu on this line. The Zn line 202.55 nm can be used, if the interference from Mg 202.58 nm is small. $ZnCl_2$ in soil can be dissolved in water then measured by ICP-AES.

Zinc oxide ZnO

The solubility of zinc oxide in water is very small, about 0.00016 g/100 c.c. at 25^{0}C. The maximum concentration of Zn in water is about 1 ppm, and may be detectable by ICP-AES using Zn lines (213.68, 202.55, 206.20 nm), if there are no significant interferences from other elements. Zinc oxide in soil can be dissolved by dilute mineral acid then measured by ICP-AES.

Zinc phosphate Zn$_3$(PO$_4$)$_2$

Zinc phosphate is not soluble in water, it may not be directly detectable from water by ICP-AES. Zinc phosphate in soil can be dissolved by dilute mineral acid then measured by ICP-AES using Zn lines (213.86, 202.55, 206.20 nm) and P lines (178.29, 213.62, 214.91 nm).

Zinc sulfate ZnSO$_4$

Zinc sulfate in water can be easily measured by ICP-AES using Zn lines (213.86, 202.55, 206.20 nm) and S lines (180.70, 182.04 nm). Zinc sulfate in soil can be dissolved by water then measured by ICP-AES.